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U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards



# Crystal Structure Transformations in Inorganic Sulfates, Phosphates, Perchlorates, and Chromates



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Issued November 1975

**Library of Congress Cataloging in Publication Data**

Rao, Chintamani Nagesa Ramachandra.

Crystal Structure Transformations in Inorganic Sulfates, Phosphates, Perchlorates, and Chromates.

(Nat. Stand. Ref. Data Ser.; NSRDS-NBS 56)

"National Standard Reference Data System."

Supt. of Docs. No.: C 13.48:56

1. Crystals. 2. Phase Rule and Equilibrium. 3. Chemistry, Inorganic. I. Prakash, Brahm, 1912-joint author. II. Title. III. Series: United States. National Bureau of Standards. National Standard Reference Data Series; NSRDS-NBS 56.

QC100.U573 No. 56 [QD921] 389'.6'08s [548'.81] 75-619082

**NSRDS-NBS 56**

Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 56, 38 pages (Nov. 1975)

CODEN: NSRDAP

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U.S. GOVERNMENT PRINTING OFFICE  
WASHINGTON: 1975

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For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402  
(Order by SD Catalog No. C13.48:56). Price 85 cents. (Add 25 percent additional for other than U.S. mailing).  
Stock Number 003-003-01396-0



## Foreword

The National Standard Reference Data System provides access to the quantitative data of physical science, critically evaluated and compiled for convenience and readily accessible through a variety of distribution channels. The System was established in 1963 by action of the President's Office of Science and Technology and the Federal Council for Science and Technology, and responsibility to administer it was assigned to the National Bureau of Standards.

NSRDS receives advice and planning assistance from a Review Committee of the National Research Council of the National Academy of Sciences-National Academy of Engineering. A number of Advisory Panels, each concerned with a single technical area, meet regularly to examine major portions of the program, assign relative priorities, and identify specific key problems in need of further attention. For selected specific topics, the Advisory Panels sponsor subpanels which make detailed studies of users' needs, the present state of knowledge, and existing data resources as a basis for recommending one or more data compilation activities. This assembly of advisory services contributes greatly to the guidance of NSRDS activities.

The System now includes a complex of data centers and other activities in academic institutions and other laboratories. Components of the NSRDS produce compilations of critically evaluated data, reviews of the state of quantitative knowledge in specialized areas, and computations of useful functions derived from standard reference data. The centers and projects also establish criteria for evaluation and compilation of data and recommend improvements in experimental techniques. They are normally associated with research in the relevant field.

The technical scope of NSRDS is indicated by the categories of projects active or being planned: nuclear properties, atomic and molecular properties, solid state properties, thermodynamic and transport properties, chemical kinetics, and colloid and surface properties.

Reliable data on the properties of matter and materials are a major foundation of scientific and technical progress. Such important activities as basic scientific research, industrial quality control, development of new materials for building and other technologies, measuring and correcting environmental pollution depend on quality reference data. In NSRDS, the Bureau's responsibility to support American science, industry, and commerce is vitally fulfilled.

A handwritten signature in black ink, reading "Ernest Ambler". The signature is fluid and cursive, with the first name "Ernest" being more prominent than the last name "Ambler".

**Ernest Ambler, *Acting Director***

## **Preface**

Earlier in this series, we presented critical reviews of phase transitions in binary halides (NSRDS-NBS 41), transition metal oxides (NSRDS-NBS 49), and inorganic nitrites, nitrates, and carbonates (NSRDS-NBS 53). In this monograph, we review crystal structure transformations in inorganic sulfates, phosphates, perchlorates, and chromates based on the literature up to 1974. A review on transition metal sulfides is due to appear in *Progress in Solid State Chemistry* (Vol. 10) this year. We believe that these five reviews would adequately cover most of the important facets of crystal structure transformations in inorganic solids and indicate the nature of problems in this area. These reviews could not have been prepared but for the support and encouragement of the National Bureau of Standards.

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# Crystal Structure Transformations in Inorganic Sulfates, Phosphates, Perchlorates, and Chromates\*

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Literature dealing with crystal structure transformations of simple inorganic sulfates, phosphates, perchlorates and chromates has been critically reviewed. Data on thermodynamic, crystallographic, spectroscopic, dielectric and other properties are given. Experimental techniques employed to obtain the data are indicated and comments on the data are made wherever necessary. All pertinent references to the published literature (up to 1974) are listed.

**Key words:** Chromates; crystal structure; crystal structure transformations; perchlorates; phase transformations; phosphates; sulfates; thermodynamic data; x-ray diffraction data.

## 1. Introduction

The study of crystal structure transformations is of great importance in understanding the structure and properties of inorganic solids. As part of our programme in preparing critical reviews on the crystal structure transformations of various types of inorganic solids, we have presently carried out a survey of the transformations of inorganic salts containing tetrahedral oxy-anions such as sulfates, phosphates, perchlorates and chromates. This review is a sequel to our monograph on the crystal structure transformations in inorganic nitrites, nitrates and carbonates [1].<sup>1</sup> In earlier monographs we have presented the transformations in binary halides [2] and transition metal oxides [3].

Of the various systems reviewed in this article, the most extensive studies have been on the crystal structure transformations of inorganic sulfates. Accordingly, we have discussed this system at length. Stern and Weise [4] have reviewed the high temperature properties and decomposition of inorganic sulfates. In view of the limited information available on the crystal structure transformations in inorganic phosphates, perchlorates and chromates, we have presented the available data in tabular form.

The general theory and other aspects of phase transformations in inorganic solids have been

reviewed in the literature [5, 6] and some aspects were briefly presented in our earlier publications from NSRDS-NBS [2, 3]. We shall, therefore, not resort to any discussion of a general nature in this review. The present review covers the material published in the literature up to 1974 and lists most of the important references. All the available crystal structure data of the different phases have been given. Results of studies employing a variety of methods and properties of solids are also presented.

## References

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## 2. Units, Symbols, and Abbreviations

Å = Angstrom ( $10^{-8}$  cm)  
bar = Unit of pressure =  $10^6$  dyn/cm<sup>2</sup> =  $10^5$  pascal  
cal = Thermochemical calorie = 4.1840 Joule

<sup>1</sup>Figures in brackets indicate literature references which appear after each section.

\*Supported by the National Bureau of Standards through the Special International Program (NBS-G-77). Earlier publications by Rao and coauthors on crystal structure transformations in this series are NSRDS-NBS 41, 49, and 53.

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C	=Coulomb
eV	=Electron volt
Hz	=Hertz (cycle/second)
O <sub>e</sub>	=Oersted
$\chi$	=Magnetic susceptibility
$\epsilon'$	=Dielectric constant
$\epsilon''$	=Dielectric loss
A	=Curie constant
$\alpha$	=Seebeck coefficient
P <sub>s</sub>	=Spontaneous polarization
T <sub>c</sub>	=Curie temperature
T <sub>N</sub>	=Neél temperature
T <sub>t</sub>	=Transition temperature
T	=Temperature in kelvin (K)
$\Delta H_{tr}$	=Enthalpy of transformation
$\Delta S_{tr}$	=Entropy of transformation
$\Delta T$	=Thermal hysteresis
$\Delta V_{tr}$	=Volume change
Z	=Number of molecules per unit cell
DTA	=Differential thermal analysis
EPR	=Electron paramagnetic resonance
IR	=Infrared
NMR	=Nuclear magnetic resonance
TGA	=Thermo-gravimetric analysis

### 3. The Sulfates

#### 3.1. Alkali Metal Sulfates

All the alkali metal sulfates undergo reversible polymorphic transformations [1, 2]. With the

exception of lithium sulfate where the transformation is from a monoclinic to a cubic structure, the other alkali metal sulfates show transformations from an orthorhombic to a hexagonal phase [3] and there is a progressive increase in transition temperature and decrease in heat of transformation as we go from sodium to cesium sulfate. In table 1, we have summarized the data on the crystal structure transformations of alkali metal sulfates. Table 2 gives crystal structure data on the various phases. The II—I phase transition in alkali metal sulfates seems to have features of both first and second order transitions as revealed by the thermodynamic and structural data as well as electrical conductivity measurements [4].

Some special features of the transitions in individual alkali metal sulfates are described in the following paragraphs.

*Lithium sulfate.* The value of  $\Delta H_{tr}$  in lithium sulfate is very high compared to other alkali metal sulfates [7] and is even higher than the heat of fusion of Li<sub>2</sub>SO<sub>4</sub>. This abnormality is possibly due to the high degree of disorder in the high temperature phase [3]. Substitution by <sup>6</sup>Li isotope lowers the T<sub>t</sub> by 0.7 K [24].

Bridgman [25] did not find any high pressure transformation in Li<sub>2</sub>SO<sub>4</sub> up to 50 kbar. Pistorius [26] has, however, identified three new high pressure forms III, IV, and V. The phase diagram of Li<sub>2</sub>SO<sub>4</sub> shows the triple points at the pressures and temperatures listed below:

TABLE 1 Crystal structure transformations of alkali metal sulfates

Sulfate	Transformation	T <sub>t</sub> , K	$\Delta H_{tr}$ , kcal mol <sup>-1</sup>	$\Delta S_{tr}$ , cal mol <sup>-1</sup> K <sup>-1</sup>	References
Li <sub>2</sub> SO <sub>4</sub>	II $\rightleftharpoons$ I	859	6.5	7.6	[3, 5-8]
Na <sub>2</sub> SO <sub>4</sub>	V $\rightleftharpoons$ IV	443	0.7	1.6	[5, 9-13]
	IV $\rightleftharpoons$ III	458			
	III $\rightarrow$ I	515	1.8	3.5	
	I $\rightarrow$ II (on cooling)	509			
K <sub>2</sub> SO <sub>4</sub>	II $\rightleftharpoons$ I	858	1.94	2.27	[5, 6, 14, 15]
Rb <sub>2</sub> SO <sub>4</sub>	II $\rightleftharpoons$ I	930	0.35		[15-17]
			2.11		[6]
Cs <sub>2</sub> SO <sub>4</sub>	II $\rightleftharpoons$ I	940	0.600 $\pm$ 0.13		[6, 7, 15]
			0.50		[6]
		986			[18]
		993			[16]

TABLE 2. Crystal structure data of alkali metal sulfates

Sulfate (phases)	Crystal system	Space group	Z	Cell dimensions	References
1	2	3	4	5	6
Li <sub>2</sub> SO <sub>4</sub>					
II (298 K)	monoclinic	P2 <sub>1</sub> /a	4	$a=8.2390 \text{ \AA}$ , $b=4.9536 \text{ \AA}$ , $c=8.4737 \text{ \AA}$ , $\beta=107.98^\circ$	[19]
I	cubic	F23 or F $\bar{4}3$ m	4	$a=7.07 \text{ \AA}$	[3]
Na <sub>2</sub> SO <sub>4</sub>					
V (298 K)	orthorhombic	D <sub>2h</sub> <sup>24</sup> -Fddd	8	$a=5.863 \text{ \AA}$ $b=12.304 \text{ \AA}$ $c=9.821 \text{ \AA}$	[9]
I (514 K)	hexagonal	—	—	$a=5.405 \text{ \AA}$ $c=7.215 \text{ \AA}$	[15]
K <sub>2</sub> SO <sub>4</sub>					
II (298 K)	orthorhombic	D <sub>2h</sub> <sup>16</sup> -Pmcn	4	$a=5.772 \text{ \AA}$ $b=10.072 \text{ \AA}$ $c=7.483 \text{ \AA}$	[20]
I (858 K)	hexagonal	—	—	$a=5.85 \text{ \AA}$ $c=8.03 \text{ \AA}$	[15]
Rb <sub>2</sub> SO <sub>4</sub>					
II (298 K)	orthorhombic	D <sub>2h</sub> <sup>16</sup> -Pmcn	4	$a=7.801 \text{ \AA}$ $b=5.965 \text{ \AA}$ $c=10.416 \text{ \AA}$	[21]
I	hexagonal	D <sub>3d</sub> <sup>3</sup> -P $\bar{3}$ m1	2	$a=6.151 \pm 0.005 \text{ \AA}$ $c=8.467 \pm 0.003 \text{ \AA}$	[22]
Cs <sub>2</sub> SO <sub>4</sub>					
II (298 K)	orthorhombic	D <sub>2h</sub> <sup>16</sup> -Pmcn	4	$a=6.264 \text{ \AA}$ $b=10.95 \text{ \AA}$ $c=8.242 \text{ \AA}$	[23]
I	hexagonal			$a=6.485 \text{ \AA}$ $c=8.980 \text{ \AA}$	[18]

I/III/II	10.7 ± 0.5 kbar	877 ± 3 K
III/IV/II	14.8 ± 0.5 kbar	871 ± 3 K
III/V/IV	20.1 ± 0.7 kbar	943 ± 4 K
I/V/III	21.5 ± 0.8 kbar	986 ± 6 K

Lithium sulfate monohydrate shows endothermic transformations at 443, 853, and 1133 K due to dehydration, polymorphic transformation, and fusion, respectively [27], the last two effects being reproducible. The 853 K transformation is akin to that in anhydrous Li<sub>2</sub>SO<sub>4</sub> with a  $\Delta H_{tr}$  of 6531 cal mol<sup>-1</sup> [28]. DTA and x-ray diffraction studies by Gruver [29] confirm the reversible phase transformation around 873 K with a  $\Delta T$  of 30 K.

*Sodium sulfate.* Na<sub>2</sub>SO<sub>4</sub>(IV), stable above 443 K and below 458 K is monoclinic [9]. Above 458 K the stable phase is Na<sub>2</sub>SO<sub>4</sub>(III). Frevel [30] found Na<sub>2</sub>SO<sub>4</sub> (III) to have an orthorhombic unit cell with space group Pbnm and dimensions  $a=5.59 \pm 0.02 \text{ \AA}$ ,  $b=8.93 \pm 0.02 \text{ \AA}$ ,  $c=6.98 \pm 0.02 \text{ \AA}$  and  $Z=4$ . Dasgupta [31] has, however, reported that Na<sub>2</sub>SO<sub>4</sub> (III) is tetragonal and belongs to a space group D<sub>2d</sub><sup>12</sup>I 42,  $Z=16$ ,  $a=13.45 \text{ \AA}$  and  $c=7.879 \text{ \AA}$ . Fischmeister [15] has shown Na<sub>2</sub>SO<sub>4</sub> (III) to possess an orthorhombic unit cell at room temperature with cell dimensions close to those by Frevel [30]. Fischmeister has also reported the cell parameters for the metastable orthorhombic Na<sub>2</sub>SO<sub>4</sub> (II) to be



$a=5.775$  Å,  $b=10.073$  Å and  $c=7.481$  Å at room temperature. DTA studies of Kreidl and Simon [32] show only one high temperature transition ( $V \rightarrow I$ ) at 511 K which occurs directly and reversibly in presence of water. According to Bird [33] the high temperature transition in dry  $\text{Na}_2\text{SO}_4$  is irreversible. Rao and Gregor [34], have shown the  $V \rightarrow I$  transition to be reversible even in dry  $\text{Na}_2\text{SO}_4$ . Moreau [14] found only three of the five previously observed forms in his DTA and x-ray diffraction investigations of  $\text{Na}_2\text{SO}_4$ . Dilatometric studies by Kracek and Gibson [11] have given the volume changes in the various transitions of  $\text{Na}_2\text{SO}_4$  as follows:  $V \rightleftharpoons IV$ ,  $+0.0005 \text{ cm}^3\text{g}^{-1}$ ;  $IV \rightleftharpoons III$ ,  $-0.0034 \text{ cm}^3\text{g}^{-1}$ ;  $III \rightleftharpoons I$ ,  $+0.007 \text{ cm}^3\text{g}^{-1}$ . Kracek and Gibson point out that  $\text{Na}_2\text{SO}_4$  (II) has no region of stability at low temperatures, but if the reaction  $I \rightarrow III$  is inhibited, the  $I \rightarrow II$  transformation takes place reversibly at 509 K with a volume decrease of  $0.004 \text{ cm}^3\text{g}^{-1}$ . High temperature x-ray diffraction and thermographic studies of Khlapova [35] reveal two hexagonal phases between 723 and 873 K. This supports Wyronboff [36] who had reported a high temperature transition in  $\text{Na}_2\text{SO}_4$  around 773 K. Simanov and Kirkina [37] have found a new orthorhombic form of  $\text{Na}_2\text{SO}_4$  at 993 K. A departure from linearity in the enthalpy versus temperature curve above 837.4 K was observed by Popov and Ginzburg [38]. The effect was more clear in their mean specific heat versus temperature curve which was interpreted as evidence for yet another polymorphic transformation. High temperature specific heat investigations of Schmidt and Sokolov [39] showed an anomaly between 963 and 993 K, with a  $\Delta H_{tr}$  of  $0.01 \text{ kcal mol}^{-1}$ . This transformation is given as  $\text{Na}_2\text{SO}_4$  (I)  $\rightarrow \delta - \text{Na}_2\text{SO}_4$ .

Bridgman [40] studied  $\text{Na}_2\text{SO}_4$  at pressures up to 50 kbar and temperatures up to 448 K. He encountered sluggish transitions around 10 kbar and 27 kbar, corresponding to  $V/III$  and  $III/VI$  transformations, respectively. High pressure DTA studies by Pistorius [41] up to 45 kbar and 723 K have revealed two new phases VII and VIII. The phase diagram shows the triple points at the pressures and temperatures indicated below:

V/IV/III	$1.5 \pm 1.5$ kbar	$446 \pm 13$ K
I/III/VII	$13 \pm 1$ kbar	$603 \pm 8$ K
III/VI/VII	$22.5 \pm 1$ kbar	$548 \pm 8$ K
I/VII/VIII	$23 \pm 1$ kbar	$678 \pm 8$ K

*Potassium sulfate.* Pannetier and Gaultier [42] reported expansion discontinuities at 533 K in  $a$  and  $c$  parameters, at 633 K in  $a$  and  $b$  parameters and at 733 K in  $a$ ,  $b$ , and  $c$  parameters. These variations, however, did not affect the orthorhombic structure of  $\text{K}_2\text{SO}_4$ .

$\text{K}_2\text{SO}_4$  was found to undergo some changes at 573, 623, 723 K, and possibly at 663 K [43–45]. Moreau [14] however, detected only two transformations at 623 K and 723 K, respectively. The electrical conductivity measurements of Ramasastry and Acharyulu [46] show an anomaly at 678 K. Watanabe et al. [47] have found the dielectric constant of  $\text{K}_2\text{SO}_4$  to increase with increasing temperature resulting in a maximum around 873 K. The electric conductivity shows an ionic behaviour above 740 K with an activation energy of 0.8 eV. On heating  $\text{K}_2\text{SO}_4$ , significant changes of the relative intensities of the diffuse and Laue maxima take place well below the transition temperature [48]. It seems that the transition is preceded by a pre-transition in a broad temperature interval. Structural changes observed are not caused by the nuclei of the new phase, but by a structural intermediate between the low and high temperature modification. There is very little indication of the pretransition effect in  $\text{K}_2\text{SO}_4$  immediately below  $T_t$ , as shown by the calorimetric measurements of Dworkin and Bredig [49]. According to them  $\Delta H_{tr}$  is  $2020 \pm 80 \text{ cal mol}^{-1}$  and  $\Delta S_{tr}$  is  $2.3 \text{ cal mol}^{-1} \text{ deg}^{-1}$ .

Up to 1 kbar the results of Majumdar and Roy [45] and Pistorius [50] are almost identical. The transition line rises linearly with pressure to 22.6 kbar and 1263 K where the slope undergoes a sharp change. This change in slope indicates a splitting of the  $II/I$  phase boundary and the appearance of  $\text{K}_2\text{SO}_4$  (III). Pistorius and Rapoport confirm that  $\text{K}_2\text{SO}_4$  (II) at 853 K differs crystallographically from the room temperature phase. They, however, do not observe the higher order transformations around 573, 623, and 723 K in the high pressure DTA.

*Rubidium sulfate.* The discontinuities observed in the thermal coefficients of the lattice parameters and volume indicate the existence of two new low energy transitions around 648 K and 848 K and a very low energy transformation at 548 K besides the usual  $II \rightleftharpoons I$  transformation [51].

*Cesium sulfate.* DTA, dilatometric and crystallographic investigations by Auby et al. [52] have established a weak transformation probably of

first order around 593 K with  $\Delta T \sim 30$  K. They also found a second order transformation around 733 K. The  $\text{II} \rightarrow \text{I}$  transformation at 933 K was accompanied by a slight change in volume [52]. With increasing temperature the  $a$  parameter was found to undergo a much larger dilation (8.264–8.882 Å) than the  $b$  (10.977–11.152 Å) and the  $c$  (6.276–6.433 Å) parameters [53]. The electrical conductivity of  $\text{Cs}_2\text{SO}_4$  was found to be enhanced above 723 K [54] possibly due to the  $\text{II} \rightarrow \text{I}$  transition.

### 3.2. Ammonium Sulfate

The room temperature phase of  $(\text{NH}_4)_2\text{SO}_4$  has an orthorhombic unit cell space group Pnam,  $Z = 4$ ,  $a = 7.73$  Å,  $b = 10.50$  Å, and  $c = 5.95$  Å [55]. Ammonium sulfate undergoes a polymorphic transformation around 223 K as shown by various techniques [56–63]. Mathias and Remeika [64] discovered that below 223 K  $(\text{NH}_4)_2\text{SO}_4$  is ferroelectric parallel to the  $a$ -axis,  $P_s$  and  $E_c$  at 215 K being  $0.254 \mu\text{C cm}^{-2}$  and  $2.0 \text{ kV cm}^{-1}$ , respectively. Kamiyashi and Miyamoto [65], however, reported the transformation to occur in the temperature range 237–244 K for single crystals and around 220 K for polycrystalline material. Singh [66] has studied the crystal structures of the room-temperature as well as the low-temperature phases of  $(\text{NH}_4)_2\text{SO}_4$ . The refinement of the room-temperature structure indicates that the actual crystal is a statistical mixture of two enantiomorphic states, the true symmetry being Pna2<sub>1</sub> rather than Pnam. Neutron diffraction studies of Singh [66] have shown that two ammonium ions which are crystallographically unrelated also have different surroundings.  $\text{NH}_4^+(\text{I})$  involves a hindered rotation at room temperature about the polar  $c$ -axis and its rotation persists below the  $T_t$ .  $\text{NH}_4^+(\text{II})$  is disordered around the plane at  $Z = \frac{1}{4}$  above the  $T_t$  and is ordered below. In the low temperature phase,  $\text{NH}_4^+(\text{II})$  shows five H-bonds of normal strength which are responsible for the dielectric polarization of ammonium sulfate. Numerous experimental results [67–69] lead to the conclusion that the transformation in  $(\text{NH}_4)_2\text{SO}_4$  is of first order.

Results of dielectric measurements on  $(\text{NH}_4)_2\text{SO}_4$  by different workers are not entirely in agreement. Hoshino et al. [67] notice an unusual shape of the dielectric constant versus temperature curve. The dielectric constant measured in the direction of the ferroelectric  $c$  axis was found not to depend on temperature in the paraelectric phase. Koptsik et al. [68], however, show the dielectric constant to

have a weak linear temperature dependence above  $T_t$ . On the contrary, Unruh [70] and Oshima and Nakamura [71] have observed that the behaviour of dielectric constant is governed by the Curie-Weiss law above  $T_t$  ( $T_c$ ). Couture-Mathieu et al. [62] and Freymann [61] find a normal behaviour at high frequencies (i.e., the dielectric behaviour shows a radical change at some frequency between 10 kHz and 24 GHz); the lower limit of frequencies at which  $(\text{NH}_4)_2\text{SO}_4$  exhibits a normal type of dielectric behaviour occurs in MHz region [67]. The rate of warming and cooling the crystal near  $T_t$  markedly affects the shape of the low frequency  $\epsilon$  versus temperature curve. Thus, with an extremely slow rate of temperature variation, normal dielectric behaviour is observed [72]. Bodi et al. [73] have studied the behaviour of the complex dielectric constant of unirradiated and gamma-irradiated ferroelectric ammonium sulfate in the microwave region as a function of temperature. They find  $T_t$  to shift from 238 K to 226 K for the irradiated sample.  $T_t$  is also affected by the application of a dc electric field along the [110] direction of the crystal [74] and by the pressure under which the study is made [75]. Hoshino et al. [67], however, could not detect any noticeable shift of  $T_t$  by any of the above effects. These authors report spontaneous polarization below  $T_t$  not to depend on temperature. Ikeda et al. [76] show that the anomalous temperature dependence of the dielectric constant, spontaneous polarization, spontaneous strain and elastic compliance can be explained in terms of the temperature dependence of the order parameter. Unruh [77] has found the spontaneous polarization to strictly depend on temperature. The  $\text{NH}_4^+$  ions in the paraelectric phase oscillate with large amplitudes and this continues even in the ferroelectric phase. At lower temperatures than  $T_t$ ,  $\text{NH}_4^+$  ions show dual behaviour [78]. Consequently, changes in the orientation of dipoles are related to  $\text{NH}_4^+(\text{I})$  and  $\text{NH}_4^+(\text{II})$  ions and they can possibly affect the orientation of  $\text{SO}_4^{2-}$  ion with change in temperature. This leads to a temperature dependent  $P_s$  [79]. The lattice parameters and birefringence of  $(\text{NH}_4)_2\text{SO}_4$  also show anomalous dependence on temperature [67, 80]. Anistratov and Martynov [81] show that the anomalies in birefringence at the  $T_c$  (or  $T_t$ ) are due to the spontaneous deformation of the crystal. Around  $T_t$ , electrical conductivity increases possibly because of the formation of cracks in the crystal near the transition [82].



Blin and Levstek [83], from their studies of NMR and IR spectra have suggested that above 173 K the  $\text{NH}_4^+$  groups reorient about random axes with a frequency higher than  $10^5$  Hz. There is no change at  $T_t$ , but a line-width transition occurs below 163 K. Below  $T_t$ , two components can be resolved, which have been interpreted as being due to “frozen in” and rotating  $\text{NH}_4^+$  ions, respectively. In the IR spectrum of  $(\text{NH}_4)_2\text{SO}_4$  [84], the splitting of the wide band at  $3235\text{ cm}^{-1}$  into a doublet (with components at  $3190$  and  $3290\text{ cm}^{-1}$ ) below 223 K is probably due to the tunnelling of a proton along the  $\text{N}-\text{H} \dots \text{O}$  bond. A very narrow band at  $963\text{ cm}^{-1}$  also appears when  $(\text{NH}_4)_2\text{SO}_4$  transforms to the ferroelectric state. These results and the absence of Curie point shift on deuteration [67] do not permit the ferroelectric properties of the crystal to be attributed to hydrogen bonding. Schutte and Heyns [85] find that the  $2\nu_2$  line at  $\sim 3300\text{ cm}^{-1}$  disappears at  $T_t$ . In this mode of vibration, the H-atoms move on the surface of a sphere whose radius is the  $\text{N}-\text{H}$  bond distance.

Raman studies by Bazhulin et al. [86] show that the intensity of bands depend on the orientation of the crystals during excitation of the spectra by natural and polarized light. Some additional bands besides those corresponding to the internal vibration of  $\text{SO}_4^{2-}$  ion are also seen. Stekhanov and Gabrichidze [87] report that the band maximum due to valence vibrations of  $\text{NH}_4^+$ , is displaced toward the smaller frequencies by  $150\text{ cm}^{-1}$  at the transformation of the crystal through the Curie point. These authors are of the view that hydrogen bonds play an important role in the appearance of the ferroelectric effect in  $(\text{NH}_4)_2\text{SO}_4$ . Recently Jain et al. [88] from their IR studies reported that the ferroelectric phase transition in  $(\text{NH}_4)_2\text{SO}_4$  is primarily due to sudden distortion in the  $\text{SO}_4^{2-}$  ions.

Inelastic neutron scattering investigations by Rush and Taylor [89] show the rotational freedom of the ions to undergo only a very small change in passing through the transition. Bajorek et al. [90] found a jump in the variation of the elastic intensity at the  $T_t$  in their neutron scattering study. Schlemper and Hamilton [91] have arrived at the same conclusion from their neutron diffraction study. They report that the transition is not of the order-disorder type, but rather involves a change in the hydrogen bonding of the ammonium groups to the  $\text{SO}_4^{2-}$ -prime which in turn results in stronger hydrogen bonds in the ferroelectric phase. This becomes possible by a

structural change in the crystal where the symmetry plane perpendicular to the ferroelectric axis is lost in the low-temperature phase. In the high-temperature phase, while each of the  $\text{NH}_4^+$  ion has only one  $\text{H}-\text{O}$  bond of  $2\text{ \AA}$ , there are bonds of  $1.9\text{ \AA}$  in the ferroelectric phase.

From proton and neutron magnetic resonance measurements, O'Reilly and Tsang [92, 93], on the other hand, find a definite change in the dynamical behaviour of  $\text{NH}_4^+$  ions. They conclude that the phase transition in  $(\text{NH}_4)_2\text{SO}_4$  is of the order-disorder type and is caused by the ordering of distorted tetrahedral  $\text{NH}_4^+$  ions which carry a dipole moment of  $0.11\text{ D}$  relative to the crystallographic plane. Dahlborg et al. [94] commenting on the controversy of the findings of Hamilton [95] and O'Reilly and Tsang [92, 93] held that the methods used were sensitive to different intervals of time. The characteristic time of a neutron-diffraction measurement is considerably different compared to the frequency of the oscillating field ( $42\text{ MHz}$ ) employed by O'Reilly and Tsang [92]. Thus, the different results can be explained on the basis of the different time scales; further, the measurements were made at different temperatures. Dahlborg et al. [94] find the transition to be of dynamic nature. The change in the dynamics of  $\text{NH}_4^+$  ions is related to the structural change in the lattice. The transition is not sharp, but extends over some twenty degrees in the time scale seen by the neutron. Far below  $T_c$ , the ions perform translational and torsional oscillations during a time longer than  $10^{-10}\text{ s}$ . Above  $T_c$ , due to thermal fluctuations in the system, the ions are capable of performing rotational motions during a considerable length of time ( $> 5 \times 10^{-11}\text{ s}$ ). The rotational motions of adjacent groups are believed to be coupled. These authors support the view of O'Reilly and Tsang [92, 93] that the transition is of order disorder type.

Nuclear spin-lattice relaxation studies of  $(\text{NH}_4)_2\text{SO}_4$  reveal a definite change in the proton relaxation behaviour in the neighbourhood of the Curie point ( $T_t$ ) indicating a change in the state of motion at the transition. The results suggest that the ferroelectric transition in  $(\text{NH}_4)_2\text{SO}_4$  is accompanied by a change in lattice structure which alters the potential in which the nuclei move, but does not involve an important change in the degree to which nuclei must cooperate in order to surmount the potential barriers [96]. Jain and Bist [79] recently developed a point charge model to compute the spontaneous polarization ( $P_s$ )  $\sim 0.42\text{ }\mu\text{C cm}^{-2}$  which

agrees well with the experimental value reported by Hoshino et al. [6]. According to them [79]  $\text{SO}_4^{2-}$  ions also contribute to the total spontaneous polarization of  $(\text{NH}_4)_2\text{SO}_4$ .

The crystal structure as well as the physical properties of  $(\text{ND}_4)_2\text{SO}_4$  are similar to  $(\text{NH}_4)_2\text{SO}_4$  [67, 97, 98].

### 3.3. Alkaline Earth Metal Sulfates

Among the alkaline earth metal sulfates,  $\text{BeSO}_4$  exhibits two polymorphic transformations while all the other sulfates undergo one transformation. The size of the ions seems to be the major factor controlling these transformations [99]. The available data on the phase transformations of alkaline earth metal sulfates are shown in the table 1. Table 2 gives the crystal structure data of the various phases.

Relevant data on some of the individual alkaline earth sulfates are presented below.

*Magnesium sulfate heptahydrate.*  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  has an orthorhombic unit cell with the space group  $D_{2h}^{21} - P2_12_12_1$ ,  $Z=4$ , and  $a=11.86 \text{ \AA}$ ,  $b=11.99 \text{ \AA}$  and  $c=6.858 \text{ \AA}$  at 298 K [111] Chihara and Seki [112] reported a phase transformation without dehydration in  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  at 362–368 K. The  $T_t$  is sensitive to external conditions and sample history. Employing radioactive isotopes, Purkayastha and Sarkar [113] reported the dehydration transition  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} \rightarrow \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  to occur at  $298 \pm 0.5 \text{ K}$ .  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  has a monoclinic unit cell with the space group  $A2/a$ ,  $Z=8$ , and  $a=24.34 \text{ \AA}$ ,  $b=7.15 \text{ \AA}$ ,  $c=10.04 \text{ \AA}$ ,  $\beta=98^\circ 34'$  [114].

*Calcium sulfate.* Naturally occurring calcium sulfate is found in two forms, gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and anhydrite ( $\text{CaSO}_4$ ). By heating gypsum at successively high temperatures, four modifications can be prepared [115]: 1,  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  (hemihydrate); 2, an extremely hygroscopic anhydrous

form (soluble anhydrite,  $\text{CaSO}_4(\text{III})$ ) which changes rapidly to hemihydrate in the presence of water vapor; 3, anhydrous modification identical to anhydrite ( $\text{CaSO}_4(\text{II})$ ), and 4, at  $\sim 1473 \text{ K}$ , a stable high temperature form ( $\text{CaSO}_4(\text{I})$ ) which decomposes afterwards.

$\text{CaSO}_4(\text{III})$  is a metastable phase and under equilibrium conditions, transformation takes place directly to  $\text{CaSO}_4(\text{II})$ . Flörke [108] and Newmann [115] have shown that  $\text{CaSO}_4(\text{I})$  cannot be quenched at room temperature. A number of workers have confirmed the presence of a high temperature thermal anomaly in  $\text{CaSO}_4$  [101, 116, 117, 118]. Deer et al. [117] have pointed out that the high temperature heat effect might be associated with the onset of rotation of  $\text{SO}_4^{2-}$  ions and not with a transition to another distinct crystal structure. Gutt and Smith [102] observed a sudden lowering of birefringence on heating  $\text{CaSO}_4$  around 1473 K leading to an isotropic state. This inversion was fully reversible and reproducible provided the specimen was not heated to a temperature far exceeding the  $T_t$ . The  $\text{II} \rightarrow \text{I}$  transformation is accompanied by a considerable volume increase. Gutt and Smith [102] have concluded that the high temperature microscopic observations of a sudden change in birefringence cannot be explained by the rotation of  $\text{SO}_4^{2-}$  ions.

DTA investigations of gypsum have shown an exothermic heat effect at  $\sim 623 \text{ K}$  possibly due to  $\text{III} \rightarrow \text{II}$  transformation [119, 120]; Berry and Kuntze [121] have reported the  $T_t$  to be 665 K. This transformation does not involve a simple monotropy, but represents the precipitation of anhydrous  $\text{CaSO}_4$  with the loss of interstitial water from the phase III solid solution [122]. The decrease in volume ( $\sim 10 \text{ \AA}^3$ ) per  $\text{CaSO}_4$  formula group prohibits the subsequent rehydration of the anhydrous compound.

TABLE 1. Phase transformation data

Sulfate	Transformation	$T_t$ , K	$\Delta H_{tr}$ , kcal mol <sup>-1</sup>	$\Delta S_{tr}$ , cal mol <sup>-1</sup> K <sup>-1</sup>	References
$\text{BeSO}_4$	III $\rightarrow$ II	863–883	3.3		[8, 100]
	II $\rightarrow$ I	908–913			
$\text{MgSO}_4$	II $\rightarrow$ I	$1283 \pm 10$			[101]
$\text{CaSO}_4$	II $\rightleftharpoons$ I	1453	5.0	3.4	[5]
		1486			[102]
$\text{SrSO}_4$	II $\rightarrow$ I	$1425 \pm 5$			[5, 103]
$\text{BaSO}_4$	II $\rightarrow$ I	1422			[5]



TABLE 2. *Crystal data of the stable phases*

Sulfate	Phase (temperature)	Crystal system	Space group	<i>Z</i>	Cell dimensions	References
BeSO <sub>4</sub>	III (room temperature)	Tetragonal (body centered)	$\overline{14}$	2	$a = 4.485 \text{ \AA}$ $c = 6.90 \text{ \AA}$	[104]
	II (883 K)	Orthorhombic (pseudo tetragonal)		2	$a = 6.58 \pm 0.01 \text{ \AA}$ $b = 4.606 \pm 0.005 \text{ \AA}$ $c = 4.675 \pm 0.005 \text{ \AA}$	[8]
	I (923 K)	Cubic (face centred)			$a = 6.65 \pm 0.03 \text{ \AA}$	[8]
MgSO <sub>4</sub>	II (below $T_t$ )	Orthorhombic	$D_{2h}^{17}$ -Cmcm	4	$a = 5.182 \text{ \AA}$ $b = 7.893 \text{ \AA}$ $c = 6.506 \text{ \AA}$	[105]
	I (above $T_t$ )	Orthorhombic	$D_{2h}^{16}$ -Pbnm	4	$a = 4.742 \text{ \AA}$ $b = 8.575 \text{ \AA}$ $c = 6.699 \text{ \AA}$	[106]
CaSO <sub>4</sub>	II (299 K)	Orthorhombic	$D_{2h}^{17}$ -Cmcm	4	$a = 6.238 \text{ \AA}$ $b = 6.991 \text{ \AA}$ $c = 6.996 \text{ \AA}$	[107]
	I (above $T_t$ )	Cubic (face centred)			$a = 7.82 \text{ \AA}^*$	[108]
SrSO <sub>4</sub>	II (299 K)	Orthorhombic	$D_{2h}^{16}$ -Pnma	4	$a = 8.359 \text{ \AA}$ $b = 5.352 \text{ \AA}$ $c = 6.866 \text{ \AA}$	[109]
	I (above $T_t$ )	Cubic			$a = 7.11 \text{ \AA}^*$	[108]
BaSO <sub>4</sub>	II (299 K)	Orthorhombic	$D_{2h}^{16}$ -Pnma	4	$a = 8.878 \text{ \AA}$ $b = 5.450 \text{ \AA}$ $c = 7.152 \text{ \AA}$	[110]
	I (above $T_t$ )	Cubic			$a = 7.21 \text{ \AA}^*$	[108]

\* Changed from kx units where  $1\text{kx} = 1.00202 \text{ \AA}$ .

*Barium sulfate.* Flörke [108] has observed the II  $\rightarrow$  I transformation in the range 1343–1383 K. Hahn emanation technique has revealed  $T_t$  to be in the range 1393–1453 K on heating and 1373–1343 K on cooling [123].

### 3.4. Thallium Sulfate

The room temperature phase of  $\text{Tl}_2\text{SO}_4(\text{II})$ , has an orthorhombic unit cell, with space group  $D_{2h}^{16}$ -Pmcn,  $Z=4$  and  $a=5.923 \text{ \AA}$ ,  $b=10.66 \text{ \AA}$ ,  $c=7.828 \text{ \AA}$  [124].  $\text{Tl}_2\text{SO}_4(\text{II})$  transforms to  $\text{Tl}_2\text{SO}_4(\text{I})$  at  $765 \pm 4 \text{ K}$  [125]. In their dilatometric studies, Samen and Tammann [126] had observed in 1903 that  $\text{Tl}_2\text{SO}_4$  goes through a sharp volume change in the vicinity of 703 K. Fischmeister [127] has found that the volume change at 703 K is not accompanied

by any change in enthalpy. Urazov and Bashilova [128] in their thermographic investigations have observed the II  $\rightarrow$  I transition at 773–778 K. DTA and high temperature x-ray diffraction studies of Majumdar and Roy [45] show a hexagonal modification to be the stable polymorph above  $T_t$ , at atmospheric pressure. They report an irregular volume expansion near  $T_t$ . Majumdar and Roy [45] find the behaviour of  $\text{Tl}_2\text{SO}_4$  to be similar to that of  $\text{K}_2\text{SO}_4$ . Dworkin and Bredig [49] disagree with Majumdar and Roy in this regard. While in  $\text{K}_2\text{SO}_4$  most of the transformation occurs isothermally at  $\sim 857 \text{ K}$  ( $\Delta H_{\text{tr}} \sim 2 \text{ kcal mol}^{-1}$ ), the corresponding transformation in  $\text{Tl}_2\text{SO}_4$  has a very small isothermal part ( $\Delta H_{\text{tr}} \sim 160 \text{ cal mol}^{-1}$  at 774 K) and is predominantly a gradual pretransitional process. The differ-

ence might be attributed to the high polarizability of the  $Tl^+$  ion.

### 3.5. Lead Sulfate

DTA investigations of Gruver [29] reveal a single endothermic peak at 1158 K, apparently representing an inversion temperature in  $PbSO_4$  described earlier [129].

### 3.6. 3d Transition Metal Sulfates

At ordinary conditions, the sulfates of divalent 3d transition metals do not show any clear thermal phase transformations except for those of cobalt and zinc. Most of these sulfates undergo magnetic transitions at very low temperatures. Some of the compounds especially  $MnSO_4$ ,  $CoSO_4$ ,  $NiSO_4$ , and  $ZnSO_4$ , exhibit high pressure transformations. Table 1 and table 2 give the phase transformations and crystal data of the 3d-transition metal sulfates.

Trivalent 3d transition metal sulfates like  $Cr_2(SO_4)_3$  do not undergo any phase transitions in the anhydrous state in the temperature range 100–295 K [130]. The hydrated sulfate  $Cr_2(SO_4)_3 \cdot 18H_2O$ , however, shows possibly a second order transition around 195 K. This transition has a marked effect on the dielectric properties due to the freeing of the polar molecular groups [131]. Ferric sulfate exists in two modifications [132], one crystallizing in the rhombohedral space group  $R\bar{3}$ ,  $Z = 2$ ,  $a = 8.791 \pm 0.004$  Å,  $\alpha = 55^\circ 52'$  and the other in the monoclinic space group,  $P2_1/n$ ,  $Z = 4$ , with  $a = 8.296 \pm 0.002$  Å,  $b = 8.515 \pm 0.002$  Å,  $c = 11.600 \pm 0.002$  Å,  $\beta = 90^\circ 30'$ . Thermodynamic data for  $Fe_2(SO_4)_3$  indicate a minor transition at 800 K with  $\Delta H_{tr}$  of 540 cal mol<sup>-1</sup> [133].

Additional information regarding the phase transformation of these sulfates is given below:

*Manganese sulfate.*  $MnSO_4$  shows a magnetic phase transition at 11.5 K which is the Néel temperature ( $T_N$ ) [143]. Specific heat measurements [144] have confirmed this value of  $T_N$  and in addition show three other peaks between 5 K and 11.5 K. Two of these peaks correspond to the two phase transitions theoretically predicted by Solyom [145].

*$MnSO_4 \cdot H_2O$ .* The Néel temperature for  $MnSO_4 \cdot H_2O$  has been reported to be 16 K [143]. Date [146] has reported some anomalies in the measurements of paramagnetic resonance and susceptibilities. This sulfate showed no resonance absorption in the liquid helium temperature region but showed a strong paramagnetic resonance above liquid

nitrogen temperature. The monohydrate exhibits strong exchange interaction as seen from the narrowness of the paramagnetic resonance lines [147].

The curve of electric resistance with pressure up to 59.5 kbar at 353 K shows a sharp change in slope at  $17.1 \pm 1$  kbar. This has been attributed to freezing of a saturated aqueous solution of  $MnSO_4$  [134].

*Iron sulfate.*  $FeSO_4$  undergoes a transformation to an antiferromagnetic state at 21 K [148] and Curie-Weiss law is valid in the range 45–90 K. Specific heat measurements on  $FeSO_4 \cdot 7H_2O$  reveals a maximum at 2.3 K [149]. In the heptahydrate, Curie law is applicable between 64 and 290 K. Between 20 and 14 K, however, the susceptibility increases much less rapidly than the high temperature Curie constant would require.

*Cobalt sulfate.* In addition to the two well known phases, a third phase  $CoSO_4(III)$  was found to exist along with the form  $CoSO_4(I)$ .  $CoSO_4(III)$  is possibly monoclinic ( $P2_1/m$ ) with dimensions  $a = 4.71$  Å,  $b = 6.70$  Å,  $c = 4.75$  Å and  $\beta = 66.2^\circ$  [150]. Borovik-Romanov et al. [148] measured the magnetic susceptibility of  $CoSO_4$  in the temperature range 13 K–300 K and observed a maximum typical of an antiferromagnetic transition near 15.5 K. Curie-Weiss law is obeyed at temperatures appreciably higher than  $T_i$ , but at lower temperatures, the temperature dependence of the magnetic susceptibility deviates widely from the Curie-Weiss law in the paramagnetic range and displays an anomalously large decrease in the antiferromagnetic range. This is possibly due to the splitting of the ground state of the  $Co^{+2}$  ion by the crystalline field. Kreines [151] measured the magnetic susceptibility in the temperature range 1.3–300 K. In magnetic fields up to  $\sim 4$  kOe, the susceptibility was independent of the field intensity. The  $\chi$ -value reached a maximum along the 3 crystal axes at 12 K. Below this temperature,  $\chi$  along each axis was different. The magnetic moment reached its maximum value at 4.2 K. Borovik-Romanov and Kreines [152] showed that  $CoSO_4$  undergoes a ferromagnetic-antiferromagnetic transformation around 12 K ( $T_N$ ). Brown and Frazer [153] and Ballestracci et al. [154] reported the structure of the low and high temperature phases of  $CoSO_4$  by neutron diffraction studies, confirming the earlier x-ray diffraction results.

*Nickel sulfate.* Borovik-Romanov et al. [148] found a maximum in magnetic susceptibility at  $\sim 37$  K characteristic of an antiferromagnetic transition. Curie-Weiss law was found to be obeyed in the temperature range 45–300 K. In the 14–34

TABLE 1. Phase transformation data

Sulfate	Transition at atmospheric pressure	Transition at high pressures			Remarks	References
MnSO <sub>4</sub>		I → II	55.2 ± 3 kbar	(771 K)		[134]
		II → III	73.5 ± 3 kbar	(771 K)		
		III → IV	96.6 ± 6 kbar	(771 K)		
FeSO <sub>4</sub>		I → II	5 kbar	(1073–1123 K)	A polymorph obtained by quenching FeSO <sub>4</sub> at 1073–1123 K	[135]
CoSO <sub>4</sub>	$T_t$ , 705 ± 8 K $\Delta H_{tr}$ , 1.6 ± 0.1 kcal mol <sup>-1</sup> $\Delta S_{tr}$ , 2.3 ± 0.2 cal mol <sup>-1</sup> K <sup>-1</sup>	I → II	6.1 ± 1 kbar	(773 K)		[5, 134]
		I → III	25 ± 1 kbar	(773 K)		
		I → IV	31 ± 2 kbar	(623 K)		
		II → III	20.6 ± 1 kbar	(973 K)		
		III → IV	37.7 ± 2 kbar	(773 K)		
		IV → V	40.6 ± 2 kbar	(773 K)		
		V → VI	48.8 ± 2 kbar	(773 K)		
		VI → VII	98 ± 5 kbar	(773 K)		
NiSO <sub>4</sub>		I → II	19 ± 1 kbar	(773 K)		[134]
		I → III	25 ± 2 kbar	(573 K)		
		II → III	29 ± 1.5 kbar	(773 K)		
		III → IV	41.8 ± 2 kbar	(773 K)		
		IV → V	65 ± 3 kbar	(773 K)		
		V → VI	94 ± 5 kbar	(773 K)		
		VI → VII	106.5 ± 6 kbar	(773 K)		
		VI → VIII	108 ± 7 kbar	(943 K)		
		VII → VIII	112.3 ± 6 kbar	(773 K)		[134]
		VIII → IX	123 ± 6 kbar	(773 K)		
CuSO <sub>4</sub>		I ⇌ II	~ 50 kbar		At all temperatures between 523 K and 775 K	[134]
ZnSO <sub>4</sub>	II → I $T_t$ , 1013 K	I → II	22.8 ± 2.5 kbar	(773 K)		[5, 29, 134]
		I → III	10 kbar	(1053 K)		
		I → IV	15 kbar	(1063 K)		
		I → V	28.0 ± 1.5 kbar	(773 K)		
		II → VI	37.0 ± 2 kbar	(773 K)		
		III → IV	16.0 ± 2 kbar	(1123 K)		
		VI → VII	50.1 ± 3 kbar	(773 K)		
		VII → VIII	73.2 ± 3.5 kbar	(773 K)		
		VIII → IX	86.7 ± 4 kbar	(773 K)		
		IX → X	96.8 ± 5 kbar	(773 K)		
		X → XI	102.6 ± 6 kbar	(773 K)		



TABLE 2. *Crystal data for known phases*

Sulfate	Phase	Crystal system	Space group	Z	Cell dimensions	References
MnSO <sub>4</sub>	room temperature	orthorhombic	D <sub>2h</sub> <sup>17</sup> -Cmcm	4	$a = 5.248 \text{ \AA}$ $b = 8.048 \text{ \AA}$ $c = 6.842 \text{ \AA}$	[134]
MnSO <sub>4</sub> · H <sub>2</sub> O	room temperature	monoclinic	A2/a-C <sub>2h</sub> <sup>6</sup>	4	$a = 7.758 \text{ \AA}$ $b = 7.612 \text{ \AA}$ $c = 7.126 \text{ \AA}$ $\beta = 115^\circ 42.5'$	[136]
FeSO <sub>4</sub>	room temperature	orthorhombic	D <sub>2h</sub> <sup>17</sup> -Cmcm	4	$a = 5.261 \text{ \AA}$ $b = 8.013 \text{ \AA}$ $c = 6.454 \text{ \AA}$	[137]
FeSO <sub>4</sub> · 7H <sub>2</sub> O	room temperature	monoclinic	C <sub>2h</sub> <sup>5</sup> -P2 <sub>1</sub> /c	4	$a = 14.072 \text{ \AA}$ $b = 6.503 \text{ \AA}$ $c = 11.041 \text{ \AA}$ $\beta = 105^\circ 34'$	
CoSO <sub>4</sub>	room temperature	orthorhombic	D <sub>2h</sub> <sup>17</sup> -Cmcm	4	$a = 5.191 \pm 0.002 \text{ \AA}$ $b = 7.864 \pm 0.002 \text{ \AA}$ $c = 6.516 \pm 0.002 \text{ \AA}$	[139, 140]
	high temperature	orthorhombic	D <sub>2h</sub> <sup>16</sup> -Pnma	4	$a = 4.738 \pm 0.002 \text{ \AA}$ $b = 8.603 \pm 0.002 \text{ \AA}$ $c = 6.699 \pm 0.002 \text{ \AA}$	
NiSO <sub>4</sub>	room temperature	orthorhombic	D <sub>2h</sub> <sup>17</sup> -Cmcm	4	$a = 6.338 \pm 0.002 \text{ \AA}$ $b = 7.842 \pm 0.001 \text{ \AA}$ $c = 5.155 \pm 0.001 \text{ \AA}$	[114]
CuSO <sub>4</sub>	room temperature (299 K)	orthorhombic	D <sub>2h</sub> <sup>16</sup> -Pmnb	4	$a = 6.6982 \pm 0.0006 \text{ \AA}$ $b = 8.3956 \pm 0.0006 \text{ \AA}$ $c = 4.8291 \pm 0.0004 \text{ \AA}$	[141]
CuSO <sub>4</sub> · 5H <sub>2</sub> O	room temperature	triclinic	—	2	$a = 6.113 \text{ \AA}$ $b = 10.712 \text{ \AA}$ $c = 5.958 \text{ \AA}$ $\alpha = 97^\circ 58'$ $\beta = 107^\circ 17'$ $\gamma = 77^\circ 26'$	[114]
ZnSO <sub>4</sub>	room temperature (298 K)	orthorhombic	D <sub>2h</sub> <sup>16</sup> -Pnma	4	$a = 8.588 \text{ \AA}$ $b = 6.740 \text{ \AA}$ $c = 4.770 \text{ \AA}$	[142]

K range, the susceptibility of NiSO<sub>4</sub> in the anti-ferromagnetic state varies with temperature according to a quadratic law.

*Copper sulfate.* Anhydrous copper sulfate shows an abrupt break at 35 K in the molar susceptibility versus temperature curve [148,155] possibly due to the formation of an antiferromagnetic array in half of the Cu<sup>+2</sup> ions. The other half of the ions

remains disordered and causes an increase in the susceptibility. Curie-Weiss law is valid in the temperature range 40–300 K. Kido and Watanabe [156] have found the Curie-Weiss law to be valid in the temperature range 90–600 K.

*CuSO<sub>4</sub> · 5H<sub>2</sub>O.* Taylor and Klug [157] discovered three polymorphic transformations at 302, 308, and 326.7 K, respectively. Expansion coefficient and

DTA measurements [158, 159] confirmed all these transitions to be second order. High temperature DTA investigations between 548 and 998 K [160] show no thermal anomaly. A number of workers [161–164] have observed DTA peaks related to the dehydration of pentahydrate. Kiriya and Ibamoto [165] measured the temperature dependence of the dielectric constant and losses of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in the temperature range 93–393 K and found distinct dispersion of the dielectric constants at temperatures higher than 343 K. Geballe and Giaque [166] showed that the magnetic system orients under the restraining influence of directional crystal forces causing changes in internal energy. The heat capacity curve has a maximum at 1.35 K, a minor maximum at 0.75 K and possibly a third maximum at 0.25 K. Dehaas and Gorter [167] measured the magnetic susceptibility in the temperature range 14.3–290 K, and found Curie-Weiss law to hold good. The measurements of magnetic anisotropy of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  at different temperatures from 83 K to 299 K [168] revealed the crystal to be nearly magnetically uniaxial with its two principal susceptibilities conforming roughly to the Curie law with different Curie constants. Magnetic measurements down to 1.6 K [169] show this salt to approximately follow Weiss law with  $\theta = -0.7^\circ$  over the whole temperature range. Benzie and Cook [170] found that the susceptibilities measured in different directions with respect to the crystallographic axes follow a Curie-Weiss law. The discrepancy between these and previous results [168] were attributed to temperature independent paramagnetism.

*Zinc sulfate.* DTA investigations of Gruver [29] on  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (natural) show two endothermic effects at 473 K and 623 K, possibly due to the loss of water of hydration. A reversible inversion is reported for anhydrous  $\text{ZnSO}_4$  at 1013 K.

### 3.7. 4d Transition Metal Sulfates

Silver sulfate exhibits a polymorphic transformation (II  $\rightarrow$  I) while  $\text{CdSO}_4$  is reported to have two polymorphic transformations (III  $\rightarrow$  II  $\rightarrow$  I). Data on phase transformations as well as the crystal structures of known phases are given in tables 1 and 2.

TABLE 1. Phase transformation data

Sulfate	Transformation	$T_i$ , K	$\Delta H_{tr}$ , kcal mol <sup>-1</sup>	$\Delta S_{tr}$ , cal mol <sup>-1</sup> K <sup>-1</sup>	References
$\text{Ag}_2\text{SO}_4$	II $\rightleftharpoons$ I	685	1.9	2.8	[5]
$\text{CdSO}_4$	III $\rightleftharpoons$ II	773			[171]
	II $\rightarrow$ I	1073			[172]

Additional information regarding these sulfates is given below.

*Silver sulfate.* Hedvall et al. [175] reported a higher  $T_i$  ( $703 \pm 3$  K) from their DTA measurements, the  $T_i$  being independent of the heating rate. On cooling, the high temperature form could be supercooled up to  $20^\circ$  below  $T_i$ . Johansson's studies [176] indicate a heterogeneous process of nucleation during this transition. Once started, the

TABLE 2. Crystal data for known phases

Sulfate	Phase (temp)	Crystal class	Space group	Z	Cell dimensions	References
$\text{Ag}_2\text{SO}_4$	II (298 K)	orthorhombic	$D_{2h}^{24}$ -Fddd	8	$a = 5.8167 \text{ \AA}$ $b = 12.704 \text{ \AA}$ $c = 10.269 \text{ \AA}$	[173]
$\text{CdSO}_4$	III (298 K)	orthorhombic	$D_{2h}^{13}$ -Pmmn	2	$a = 4.7174 \text{ \AA}$ $b = 6.5590 \text{ \AA}$ $c = 4.7012 \text{ \AA}$	[174]
$\text{CdSO}_4$	I	orthorhombic			$a = 5.310 \text{ \AA}$ $b = 8.157 \text{ \AA}$ $c = 7.180 \text{ \AA}$	[172]

transition proceeds very fast in a given crystal. The transition could not be induced by contact with the low temperature form above 698 K. At the II→I transition, the electrical conductivity of  $\text{Ag}_2\text{SO}_4$  was found to increase rapidly by approximately one decimal power [177]. Vesnin [178] reported an enantiotropic transformation around 843 K. He found this transformation to be rather slow.

**Cadmium sulfate.** Maksimova [171] detected two peaks in the DTA heating curves for  $\text{CdSO}_4$ . Specimens prepared by different methods produce different thermograms possibly due to difference in crystal structure. Maksimova found that  $\text{CdSO}_4(\text{III})$  is non-homogeneous and consists of two types of aggregates with different refractive indices. Heterogeneity was observed only in specimens whose thermograms show the double thermal effects. From the heating and cooling curves of  $\text{CdSO}_4$  Sholokovich and Zvorykina [179] showed a new transformation in the range 1119–1125 K.

### 3.8. Rare Earth Metal Sulfates

Thermal anomalies in hydrated rare earth metal sulfates have been reported by a number of workers [180–185] which are mostly attributed to the loss of water of hydration. Zaitseva [186] from thermographic, thermogravimetric, spectroscopic and x-ray diffraction studies, showed  $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  to have one polymorphic transformation in the temperature range 678–738 K which could not be related to the loss of water of hydration. Around 573 K, the hydrated sulfate was found to change to an anhydrous cubic modification ( $a = 6.63 \pm 0.01 \text{ \AA}$ ), which on further heating changed to an equilibrium macrocrystalline state (678 K). TGA thermograms did not show further weight loss in the 573–873 K range. There appeared another transformation in the crystal structure (as found from x-ray studies) above 873 K, which was not accompanied by any thermal effects. Thermograms for  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  and  $\text{Tb}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ , differ from that of  $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  in not having the exothermic effect in the temperature range 678–738 K. At 473 K the crystalline hydrates apparently possess cubic structure with  $a = 6.36 \pm 0.02 \text{ \AA}$ . Heating the octahydrate up to 573 K, leads to formation of compounds isostructural with anhydrous Eu-sulfate. For anhydrous Gd-sulfate two more polymorphic modifications were found at 823 K and 923 K, respectively. Anhydrous Tb-sulfate shows two polymorphic modifications, the first, stable over the wide temperature range,

573–873 K, having a cubic structure. The second modification at 903 K has a relatively complex crystal structure.

Room temperature crystal data for the Eu, Gd, and Tb sulfate octahydrates are given in table 1.

TABLE 1. Crystal data for some monoclinic rare earth metal sulfates [186]

Sulfate	$a$ $\pm 0.003$	$b$ $\pm 0.001$	$c$ $\pm 0.004$	$\beta$ $\pm 1^\circ$	$Z$
$\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$	13.566	6.781	18.334	$102^\circ 14'$	4
$\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$	13.544	6.774	18.299	$102^\circ 11'$	4
$\text{Tb}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$	13.502	6.751	18.279	$102^\circ 09'$	4

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## 4. The Phosphates

Substances	Measuring technique	Observations	Remarks	References
<i>Lithium phosphate</i> Orthorhombic, Pcmn $a = 6.07 \text{ \AA}$ , $b = 10.26 \text{ \AA}$ , $c = 4.86 \text{ \AA}$ (stable phase)	Crystallographic studies	$T_i$ , 775 K Low $\text{Li}_3\text{PO}_4$ has the $\beta_{  }$ structure while high $\text{Li}_3\text{PO}_4$ has the $\gamma_{  }$ structure. The $\beta$ -phase is stable at RT.	High temperature $\gamma$ -phase can be preserved metastably at ambient conditions by rapid cooling.	[1, 2]
<i>Sodium phosphate</i> tetragonal $a = 10.81 \text{ \AA}$ $c = 6.84 \text{ \AA}$ (stable phase)	Crystallographic and dielectric measurements	$T_i$ , 473–573 K Low temperature form ( $\alpha$ ) transforms to high temperature form ( $\gamma$ ). Between 110 and 180 K very rapid increase of $\epsilon''$ occurs.	The $\gamma$ -phase is cubic with $a = 7.56 \text{ \AA}$ at 873 K.	[3, 4]
<i>Ammonium phosphate</i> $(\text{NH}_4)_3\text{PO}_4$	NMR	$T_i$ , 193 K The spectrum changes from a single line at RT to two components at temperatures below $T_i$ .	These components belong to frozen in and rotating $\text{NH}_4^+$ ions.	[5]

#### 4. The Phosphates – Continued

Substances	Measuring technique	Observations	Remarks	References
<i>Calcium phosphate</i> $\alpha$ - $\text{Ca}_3(\text{PO}_4)_2$ , monoclinic, $P2_1/a$ , $Z=8$ , $a=13.07 \text{ \AA}$ , $b=9.11 \text{ \AA}$ , $c=12.86 \text{ \AA}$ , $\beta=108^\circ 9'$ (stable phase)	Dielectric constant and loss	At 262 K, an abrupt, almost discontinuous increase is observed.		[4]
	High pressure studies up to 40 kbar	Details not available		[6]
	Crystallographic studies	$T_i$ , 1453 K	High temperature form $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$ is hexagonal,	[7, 8]
	Luminescence and calorimetric measurements	Anomalies at 233 and 308 K appear in these measurements.	$R\bar{3}c$ , $Z=8$ with $a=10.345 \text{ \AA}$ and $c=36.905 \text{ \AA}$ .	[8]
<i>Boron phosphate</i> $\text{BPO}_4$ , hexagonal $a=4.332 \text{ \AA}$ $c=6.640 \text{ \AA}$ (low cristobalite form, stable phase)	High pressure studies	$\text{BPO}_4$ transforms from a cristobalite to a quartz form at 46 kbar	High pressure form is quartz like hexagonal with $a=4.470 \pm 0.005$ , $c=9.926 \pm 0.01 \text{ \AA}$ and $Z=3$ .	[9–11]
		Investigations up to 85 kbar at temperature range 1273–1473 K show a dense modification of $\text{BPO}_4$ .	The dense modification has the cell dimensions $a=7.75 \pm 0.02 \text{ \AA}$ , $c=9.95 \pm 0.02 \text{ \AA}$ and $Z=9$ .	
<i>Aluminium phosphate</i> $\text{AlPO}_4$ , hexagonal, $P3_1$ , $Z=3$ , $a=4.92 \text{ \AA}$ , $c=10.91 \text{ \AA}$ (berlinite form, stable phase)	Crystallography and TGA	$T_i$ , 854 (rhombohedral to hexagonal) $T_i$ (rev) 847 K; $\Delta H_{tr}$ , 2.64 cal $\text{g}^{-1}$ ; $\Delta V_{tr}$ , +0.88 $\text{\AA}^3$	The transformation involves dilation in the $c$ -direction as in quartz. The crystal data for other forms are as follows: <i>low cristobalite</i> : orthorhombic, $C22_1$ , $Z=4$ , $a=7.099 \pm 0.003 \text{ \AA}$ $b=7.099 \pm 0.003 \text{ \AA}$ $c=7.006 \pm 0.003 \text{ \AA}$ tetragonal, $I\bar{4}$ , $Z=2$ , $a=4.99 \text{ \AA}$ $c=6.90 \text{ \AA}$ <i>Cristobalite</i> , cubic, $Z=4$ , $a=7.11 \pm 0.01 \text{ \AA}$ at 623 K.	[1, 10, 12]
		Three distinct modifications of $\text{AlPO}_4$ are obtained; tridymite, cristobalite and berlinite (quartz structure). The $T_i$ 's are 363 K, 493 K, and 853 K, respectively.	The tridymite and cristobalite forms were not found to convert back to the berlinite on prolonged heating.	
	EPR of $\text{AlPO}_4:\text{Fe}^{+3}$	The transformation is confirmed.		[16]
	Raman spectroscopy	Confirmed the transformation.	$\text{AlPO}_4$ has a complicated soft mode lying at reciprocal lattice points in $\text{AlPO}_4$ . These are Raman active. One such mode is at $158 \text{ cm}^{-1}$ and is totally symmetric.	[17]
	Crystallographic and DTA studies			[13–15]

## 4. The Phosphates – Continued

Substances	Measuring technique	Observations	Remarks	References
	High pressure investigations	Pressure-temperature curve for the quartz-tridymite transformation, determined up to 1 kbar gave $\Delta H_{tr}$ , $\sim 262$ cal mol <sup>-1</sup> . Polymorphic transformation near 55 kbar and 723 K. At 1173 K and 60 kbar two new forms entirely different from the known forms were obtained.		[10, 18, 19]
		The 1273 K and 100 kbar, a third form was found.	The third new form at 1273 K and 100 kbar has the crystal data: $a = 5.11$ Å, $b = 7.48$ Å, $c = 6.09$ Å.	
<i>Gallium phosphate</i> GaPO <sub>4</sub> , hexagonal, P3 <sub>1</sub> , $Z = 1$ , $a = 4.902$ Å, $c = 11.05$ Å (stable phase)	Crystallographic studies and DTA	GaPO <sub>4</sub> was found to exhibit three phases: 1. berlinite (low quartz) 2. low cristobalite 3. high cristobalite Two phase transformations were detected corresponding to DTA peaks. a. berlinite $\rightarrow$ high cristobalite (a slow change) at 1243–1253 K. b. low-cristobalite $\rightarrow$ high cristobalite (a rapid and reversible change) at 886–896 K on heating and 843–	The cristobalite form of GaPO <sub>4</sub> can be easily converted to the berlinite type by proper heat treatment.  The low cristobalite form is orthorhombic C222 <sub>1</sub> , $Z = 4$  $a = 6.967 \pm 0.003$ Å $b = 6.967 \pm 0.003$ Å $c = 6.866 \pm 0.003$ Å	[1, 20, 21]
<i>Lead phosphate</i> Pb <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> monoclinic, C <sub>2h</sub> <sup>6</sup> –C2/c $Z = 4$ $a = 13.816$ Å $b = 5.692$ Å $c = 9.429$ Å and $\angle = 102.36^\circ$ (stable phase)	Crystallographic studies.	Low temperature monoclinic phase transforms to the high temperature around 473 K.	The high temperature form (I) has orthorhombic unit cell, D <sub>3d</sub> <sup>2</sup> –R $\bar{3}$ m $Z = 1$ , $a = 5.53 \pm 0.02$ Å $c = 20.30 \pm 0.05$ Å at $473 \pm 15$ K.	[22, 23]
	Heat capacity	Measurements between 15 and 300 K did not show any anomaly.		[24]
<i>Bismuth phosphate</i> BiPO <sub>4</sub> , monoclinic P2 <sub>1</sub> /n–C <sub>2h</sub> <sup>5</sup> , $Z = 4$ $a = 6.74 \pm 0.02$ Å $b = 6.92 \pm 0.02$ Å $c = 6.46 \pm 0.02$ Å $\beta = 103^\circ 30'$ (monazite type, stable phase)	Crystallographic studies	Two phases monoclinic as well as hexagonal are the stable forms at room temperature.  A third phase stable at high temperatures was also discovered.  The monazite type is the stable form of BiPO <sub>4</sub> over a wide temperature range.	The room temperature hexagonal phase has the cell dimensions $a = 6.966 \pm 0.001$ Å $c = 6.460 \pm 0.002$ Å  The high temperature phase is monoclinic with the cell dimensions $a = 4.88 \pm 0.03$ Å $b = 7.06 \pm 0.02$ Å $c = 4.71 \pm 0.03$ Å $\beta = 96.3 \pm 0.5^\circ$ space group: P2 <sub>1</sub> –C <sub>2</sub> <sup>2</sup> or P2 <sub>1</sub> /m	[25, 26]

## 4. The Phosphates – Continued

Substances	Measuring technique	Observations	Remarks	References																		
<i>Chromium phosphate</i> CrPO <sub>4</sub> (crystal data not available)	Crystallographic, DTA and hydrothermal studies	The high temperature structure slowly converts to the monazite type at ordinary temperatures. No spontaneous change from the hexagonal to the monazite type has been detected.  <i>T<sub>t</sub></i> , 1448 K (β→α) An amorphous form exists up to 1073 K. The reflections for the β-phase appear at 1223 K.	β= phase is an unstable phase and converts to α-phase gradually.	[27, 28]																		
<i>Manganese phosphate</i> ... Mn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , hexagonal <i>a</i> =4.94 Å <i>c</i> =5.48 Å (stable phase)	DTA  High pressures	<i>T<sub>t</sub></i> , 1086 ± 5 K (Quartz type phase converts to the cristobalite type)  At the pressure ~ 55 kbar and temperature 723 K, a new phase has been reported.	Cristobalite type phase has the cell dimensions: <i>a</i> = 4.97 Å, <i>c</i> = 6.97 Å	[29]  [10]																		
<i>Iron phosphate</i>	Crystallographic studies  X-ray diffraction and DTA  High pressure studies	Four varieties, orthorhombic, triclinic, monoclinic (dull red) and orthorhombic (pale green) forms were reported. The last three were, however, later found to be identical with no apparent points of transformation among themselves.  <i>T<sub>t</sub></i> , 973–983 K (reversible transformation)  Around 55 kbar and 723 K, FePO <sub>4</sub> is reported to transform to a new form.	In nature FePO <sub>4</sub> is found as strengite (orthorhombic) and phosphosiderite (monoclinic). Quartz type modification has the dimensions: <i>a</i> = 5.035 Å <i>c</i> = 5.588 × 2 Å  Several inversions reported earlier were not confirmed.	[30–32]  [29, 33]  [10]																		
<i>Zinc phosphate</i> Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> monoclinic C <sub>2h</sub> <sup>6</sup> -C2/c, <i>Z</i> = 4 <i>a</i> = 8.14 ± 0.02 Å <i>b</i> = 5.63 ± 0.01 Å <i>c</i> = 15.04 ± 0.04 Å β = 105°08' ± 05' (stable phase)	Crystallographic studies	α-Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> transforms to the β-Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> at 1215 K	β-Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> is also monoclinic with space group P2 <sub>1</sub> /c, <i>Z</i> = 4, <i>a</i> = 9.393 ± 0.003 Å <i>b</i> = 9.170 ± 0.006 Å <i>c</i> = 8.686 ± 0.003 Å β = 125.73° ± 0.10	[34, 35]																		
<i>Rare earth metal phosphates</i>	Crystallographic studies	La, Ce, Pr, Nd, Sm, Eu, Gd, and Tb-phosphates have monazite type structure. Some of them also possess a hexagonal structure at RT. This hexagonal α-phase transforms to β-phase on heating between 673 and 1073 K. Dy-, Ho-, Er-, Tin-, Yb-, and	<i>Crystal data</i> (hexagonal) <i>Z</i> = 3, space group P3 <sub>1</sub> 21(D <sub>3</sub> <sup>4</sup> )  <table><tr><td><i>Phosphate</i></td><td><i>a</i></td><td><i>c</i></td></tr><tr><td>La-</td><td>7.081</td><td>6.468</td></tr><tr><td></td><td>±0.005 Å</td><td>±0.008 Å</td></tr><tr><td>Ce-</td><td>7.055</td><td>6.439</td></tr><tr><td></td><td>±0.003 Å</td><td>±0.005 Å</td></tr><tr><td>Nd-</td><td>7.00</td><td>6.39</td></tr></table>	<i>Phosphate</i>	<i>a</i>	<i>c</i>	La-	7.081	6.468		±0.005 Å	±0.008 Å	Ce-	7.055	6.439		±0.003 Å	±0.005 Å	Nd-	7.00	6.39	[36–39]
<i>Phosphate</i>	<i>a</i>	<i>c</i>																				
La-	7.081	6.468																				
	±0.005 Å	±0.008 Å																				
Ce-	7.055	6.439																				
	±0.003 Å	±0.005 Å																				
Nd-	7.00	6.39																				



## 4. The Phosphates—Continued

Substances	Measuring technique	Observations	Remarks	References
		Lu-phosphates have zircon type structure (tetragonal, space group $C_{2h}^{19}$ ). Tb-phosphate also exists in zircon type structure.	$\pm 0.01 \text{ \AA}$ $\pm 0.03 \text{ \AA}$ Gd-      6.89      6.32 $\pm 0.01 \text{ \AA}$ $\pm 0.02 \text{ \AA}$ <i>Monoclinic monazite type,</i> $P2_1/n-C_{2h}^5, Z=4$  <i>Phosphate</i> <i>a</i> <i>b</i> <i>c</i> $\beta$ La      6.83   7.05   6.48 $103^\circ 34'$ Ce      6.76   7.00   6.44 $103^\circ 38'$ Pr      6.75   6.94   6.40 $103^\circ 21'$ Nd      6.71   6.92   6.36 $103^\circ 28'$	
	Crystallographic studies	Phase transformations in $\text{SmPO}_4$ and $\text{PrPO}_4$ have been found at 873 K. Above 773 K, $\text{YbPO}_4$ undergoes a phase transition like $\text{SmPO}_4$ and $\text{PrPO}_4$ .	The x-ray diffraction pattern of $\text{YbPO}_4$ after being heated at 1273 K is different from the corresponding patterns of $\text{SmPO}_4$ and $\text{PrPO}_4$ . This high temperature phase is tetragonal, space group $I4_1/amd (D_{4h}^{19})$ with $a=6.812 \text{ \AA}$ , $c=5.973 \text{ \AA}$ .	[40]
	Magnetic measurements	The $T_i$ 's in magnetically ordered rare-earth compounds, which have no conduction electrons, are considerably low because of the weak exchange interactions between rare-earth ions.	The Gd-, Tb-, and Dy-phosphates were found to have extremely high Neél temperatures of 225 K, 415 K, and 505 K respectively. Saji et al. [42], however, differ from earlier results of Wang et al. [41] suggesting antiferromagnetic transitions.	[41–43]
<i>Erbium phosphate</i>	Magnetic measurements	From the temperature dependence of the susceptibility in the low temperature region where only the lowest doublet is populated, a Curie temperature of $-1 \text{ K}$ is extrapolated. This would place a transition to an antiferromagnetically ordered state below 1 K.	A similarly low $T_i$ of 0.8 K has been calculated from the estimated dipole interaction, indicating that the exchange interaction is very small or negligible compared to the dipole interaction. $\text{ErPO}_4$ , therefore, may be a good example of a pure dipolar magnetic ordering.	[44]
<i>Terbium phosphate</i>	Specific heat and magnetic measurements	<p>The plot of the specific heat versus temperature shows two <math>\lambda</math>-type anomalies. One at the Neél point (<math>T_N</math>), <math>2.20 \pm 0.05 \text{ K}</math> and the other at Curie point (<math>T_c</math>), <math>3.5 \pm 0.1 \text{ K}</math>, which has to be attributed to a crystallographic phase transition from tetragonal to some lower symmetry.</p> <p>The magnetic measurements on single crystals show that there is a strong magnetic anisotropy in the plane perpendicular to the optical axis at temperatures below <math>T_c</math>.</p>	With external fields more than 7 kOe the weak and strong directions can be interchanged, giving rise to a very sharp $\pi/2$ periodicity of the magnetization perpendicular to the optical axis, if the crystal is rotated around the $c$ -axis by $2\pi$ .	[45]



## 4. The Phosphates – Continued

Substances	Measuring technique	Observations	Remarks	References
<i>Dysprosium phosphate</i>	Magnetic measurements	DyPO <sub>4</sub> is found to order antiferromagnetically at approx. 3.5 K. The transition from the antiferromagnetic to the paramagnetic state is first order, below a critical temperature $T_c$ near 0.75 K. This transition at higher temperatures is of higher order. $T_i$ (paramagnetic-antiferromagnetic) in case of DyPO <sub>4</sub> has been reported to be 2.8 K.	This appeared to be an ideal 3-dimensional Ising antiferromagnet.	[46–49]  [50]
<i>Holmium phosphate</i>	Specific heat and magnetic measurements	At 1.39 K, a magnetic phase transition is observed.		[51]

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## 5. The Perchlorates

Substance	Measurement technique	Observations	Remarks	References
<i>Lithium perchlorate</i> $\text{LiClO}_4$ Orthorhombic, Pmnb, $Z=4$ $a=6.926 \text{ \AA}$ $b=8.659 \text{ \AA}$ $c=4.836 \text{ \AA}$ (stable phase)	Crystallography and DTA	No polymorphic transformation at normal pressures.		[1-4]
	High pressure studies	A high pressure phase transition is seen around 16.4 kbar		[5]
<i>Sodium perchlorate</i> $\text{NaClO}_4$ orthorhombic, Amma, $Z=4$ $a=7.06 \pm 0.02 \text{ \AA}$ $b=7.08 \pm 0.02 \text{ \AA}$ $c=6.48 \pm 0.02 \text{ \AA}$ (stable phase)	Crystallography and DTA	$T_t$ , 577-586 K (orthorhombic $\rightarrow$ cubic) The transformation is accompanied by a volume increase $\Delta V_{tr}$ of $14.27 \text{ \AA}^3$ per molecule. There is not much hysteresis accompanying the transformation.	High temperature phase is cubic, space group: $F\bar{4}3m$ , $Z=4$ $a=7.09 \text{ \AA}$ at 587 K.	[1-4, 6, 7]
	Dielectric constants	A sharp increase in the dielectric constant at $T_t$ is observed. $\epsilon/T$ curve has a small maxima slightly before the $T_t$ .	Small anomaly just before $T_t$ is possibly due to the prerotation caused by the loosening of the lattice structure.  The sharp increase in $\epsilon$ at $T_t$ must be corresponding to the onset of free rotation of $\text{ClO}_4^-$ during the disordering of the lattice to the cubic structure.	[7, 8]
	Electrical conductivity	Thermal anomaly at $T_t$ is observed.	In $\text{NaClO}_4$ , the large difference in the ionic radii and a very high value of the $\epsilon$ in the cubic phase suggests a Frenkel type disorder.	[7]
	Thermoelectric power	A break in the $\alpha$ versus $T$ is noticed at the $T_t$ . An abrupt increase in $\alpha$ is found.		[7]
	IR spectroscopy and micro projection measurements	$T_t$ , 581 K A band around $935 \text{ cm}^{-1}$ , the symmetric stretching frequency of $\text{ClO}_4^-$ , disappears at the $T_t$ .	The transformation is reversible.	[4, 8, 9]

## 5. The Perchlorates – Continued

Substance	Measurement technique	Observations	Remarks	References
<p><i>Potassium perchlorate</i> orthorhombic, Pbnm, <math>Z = 4</math> <math>a = 7.2401 \pm 0.0023 \text{ \AA}</math> <math>b = 8.8373 \pm 0.0030 \text{ \AA}</math> <math>c = 5.6521 \pm 0.0040 \text{ \AA}</math> (stable phase)</p>	High pressure studies	NaClO <sub>4</sub> has two high pressure transitions up to 50 kbar.	NaClO <sub>4</sub> phase III, the phase stable at >30 kbar probably has a structure similar to BaSO <sub>4</sub> .	[5, 10]
	Crystallographic, DTA and dilatometric studies	$T_t$ , 573–579 (orthorhombic → cubic) with $\Delta T$ , 5.6 K. $\Delta H_{tr}$ , 3.29 kcal mol <sup>-1</sup> The transformation is accompanied by a large volume change.	The cubic phase has the crystal data as follows: space group: $F\bar{4}3m$ $Z = 4$ $a = 7.52 \text{ \AA}$ at 583 K	[1–3, 6, 11–13]
	Dielectric measurements	An increase in $\epsilon$ is observed at the $T_t$ .	Rotation of ClO <sub>4</sub> <sup>-</sup> is indicated by the results. Transformation is an order-disorder type.	[7, 8]
	Electrical conductivity	An increase in conductivity is reported at the $T_t$ .	The activation energy for the cubic phase is less than that in orthorhombic phase.	[7]
	Thermoelectric power	A break in the curve $\alpha$ vs $T$ is noticed at $T_t$ .	KClO <sub>4</sub> indicates an increase in $\alpha$ followed by a sharp decrease.	[7]
	IR spectroscopy and micro-projection	A band around 935 cm <sup>-1</sup> , observed in orthorhombic form, disappears at $T_t$ .	The transition is reversible.	[4, 8, 9]
<p><i>Rubidium perchlorate</i> RbClO<sub>4</sub>, orthorhombic, Pbnm, <math>Z = 4</math> <math>a = 7.53 \text{ \AA}</math> <math>b = 9.27 \text{ \AA}</math> <math>c = 5.81 \text{ \AA}</math> (stable phase)</p>	High pressure studies.	Orthorhombic → cubic transition line rises from 569 K at atmospheric pressure to 839 K at 11.3 kbar, where it is found to decompose explosively.	No high pressure phase exists in KClO <sub>4</sub> .	[5, 14]
	Crystallographic and DTA studies.	$T_t$ , 551–554 K	High temperature phase is cubic with space group $F\bar{4}3m$ , $Z = 4$ and $a = 7.72 \pm 0.01 \text{ \AA}$ at 573 K.	[1, 2, 6]
	Dielectric constant	A sharp increase is observed at the $T_t$ .	The transformation is an order-disorder type.	[8]
	Electrical conductivity	An increase in conductivity is observed at the $T_t$ .	Energy of activation for conduction is less in cubic phase as compared to that of orthorhombic phase.	[7]
	Thermoelectric power	RbClO <sub>4</sub> shows an increase in $\alpha$ followed by a sharp decrease after the transformation.		[7]
	IR spectroscopy and micro projection technique	$T_t$ , 552 K A band around 935 cm <sup>-1</sup> disappears at the $T_t$ .	Transformation is found to be reversible.	[4, 8]



## 5. The Perchlorates – Continued

Substance	Measurement technique	Observations	Remarks	References
<i>Cesium perchlorate</i> $\text{CsClO}_4$ , orthorhombic, Pnma, $Z=4$ $a=7.79 \text{ \AA}$ $b=9.82 \text{ \AA}$ $c=6.00 \text{ \AA}$ (stable phase)	High pressure studies.	$\text{RbClO}_4$ has a high pressure transformation near 15 kbar with a volume change of less than $1.3 \text{ cm}^3 \text{ mol}^{-1}$ .		[5, 15]
	Crystallographic, DTA and dilatometric measurements	$T_t$ , 492–497 K (orthorhombic $\rightarrow$ cubic) The transformation is accompanied by a large volume change.	The high temperature cubic phase has the space group $F\bar{4}3m$ , $Z=4$ and $a=8.00 \pm 0.02 \text{ \AA}$ at 503 K.	[1, 2, 6, 11, 13]
	Dielectric constant	$\text{CsClO}_4$ shows a sharp increase of $\epsilon$ at $T_t$ .	Order-disorder type transition is suggested.	[8]
	Electrical conductivity	An increase in conductivity of $\text{CsClO}_4$ is noticed at the $T_t$ .	The energy of activation in the cubic phase is less than that in the orthorhombic phase.	[7]
	Thermoelectric power	$\text{CsClO}_4$ shows an anomalous behaviour as $\alpha$ changes sign from negative to positive value.	$\alpha$ increases with increase in temperature in cubic $\text{CsClO}_4$ .	[7]
	High pressure studies (DTA, crystallography and volumetric technique)	$\text{CsClO}_4$ is found to have two transitions with a volume change of $3.5 \text{ cm}^3 \text{ mol}^{-1}$ in the former. The high pressure transition $\text{III} \rightarrow \text{IV}$ occurs near 1 kbar. The transitions from II and IV phases to I take place at 6.4 kbar, 692 K, and 17.1 kbar, 813 K, respectively.	<i>Triple points</i> IV/III/II 4.5 kbar 587 K I/IV/II 7.0 kbar 684 K	[5, 16]
<i>Ammonium perchlorate</i> $\text{NH}_4\text{ClO}_4$ , orthorhombic, Pbnm, $Z=4$ , $a=7.449 \pm 0.005 \text{ \AA}$ $b=9.202 \pm 0.006 \text{ \AA}$ $c=5.816 \pm 0.004 \text{ \AA}$ (stable phase)	Crystallography	$T_t$ , 513 K (orthorhombic-cubic) $\text{NH}_4\text{ClO}_4$ seems to undergo a phase transformation near 83 K also.	The cubic phase has the crystal data: space group $F\bar{4}3m$ , $Z=4$ , $a=7.69 \pm 0.02 \text{ \AA}$ at 516 K. The transformation is presumably occasioned by the onset of free rotation of $\text{ClO}_4^-$ ion. In addition $\text{NH}_4^+$ ion has also been reported to undergo free rotation.	[1, 17–21]
	DTA	$T_t$ , 513 K $\Delta T$ , 15 K	DTA thermograms change with the thermal history of the sample, and even with aging at ambient temperature.	[22]
	Heat capacity measurements	The measurement do not support earlier results showing a phase transformation at 83 K.	$\text{NH}_4^+$ ion has been found to freely rotate.	[23, 24]
	Crystallography, IR, Raman spectra	No phase transformation in 120 K–300 K range. Anomalies are seen in the temperature ranges, 20–50 K and 100–110 K.	The free rotation of $\text{NH}_4^+$ ion is also reported.	[25, 26]

## 5. The Perchlorates – Continued

Substance	Measurement technique	Observations	Remarks	References
	NMR	The results are interpreted in terms of reorientation of the $\text{NH}_4^+$ ion about random or nearly random axes.	The relaxation times are consistent with a barrier hindering reorientation of $2.0 \pm 0.6$ kcal.	[27]
	Cold neutron studies	This also supports the principle of essentially unrestricted rotational motion of the $\text{NH}_4^+$ ion in the crystal lattice.		[28]
	Optical micro-projection technique	$T_i$ , 513 K		[4]
	High pressure studies	$\text{NH}_4\text{ClO}_4$ is found to have a transformation accompanied by a volume change of $< 1.3 \text{ cm}^3 \text{ mol}^{-1}$ . The usual orthorhombic $\rightarrow$ cubic transition was followed to 4 kbar and 573 K. $\text{NH}_4\text{ClO}_4$ explodes violently in the range 603–623 K at 2–3.6 kbar although at atm. pressure it explodes only at 713 K.	The anomalous curvature of Bridgman's $\text{NH}_4\text{ClO}_4$ II/III transition line near 373 K is due to a triple point involving the phase found at atmospheric pressure below 83 K. The explosion in $\text{NH}_4\text{ClO}_4$ may be due to large volume change upon transition which causes local pressure increase at the sample. No other transitions could be detected down to 123 K at atmospheric pressures.	[5, 29]
<i>Thallium perchlorate</i> $\text{TlClO}_4$ , orthorhombic, $\text{Pbnm}$ , $Z=4$ $a=7.50 \text{ \AA}$ $b=9.42 \text{ \AA}$ $c=5.88 \text{ \AA}$ (stable phase)	Crystallographic studies	$T_i$ , 539 K (orthorhombic $\rightarrow$ cubic)	High temperature phase is cubic. space group: $\text{F}\bar{4}3\text{m}$ , $Z=4$ and $a=7.63 \text{ \AA}$	[1]
	Optical micro-projection technique	$T_i$ , 539 K	The Thallium salt is particularly more suited for microprojection demonstration as the orthorhombic form is strongly birefringent.	[4]
	High pressure studies	A high pressure phase III is found with the initial volume change $\Delta V_{\text{tr}}$ , $5 \text{ cm}^3 \text{ mol}^{-1}$ . The triple point I/III/II is at 0.7 kbar and 553 K.	Earlier, Bridgman reported the transition to accompany $\Delta V_{\text{tr}}$ , $< 1.3 \text{ cm}^3 \text{ mol}^{-1}$ .	[5, 30]
<i>Silver perchlorate</i> $\text{AgClO}_4$ , orthorhombic	Crystallographic	$T_i$ , 428 K (orthorhombic-cubic)	The high temp. cubic phase has the space group $\text{F}\bar{4}3\text{m}$ , $Z=4$ and $a=7.01 \pm 0.01 \text{ \AA}$ at 433 K.	[1]
	Optical micro-projection studies	$T_i$ , 428–432 K Another transition appears to take place at 375–383 K.	The silver salt begins decomposing near $T_i$	[4, 31]

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## 6. The Chromates

Substance	Measurement technique	Observations	Remarks	References											
<i>Sodium chromate</i> Na <sub>2</sub> CrO <sub>4</sub> , orthorhombic, Amam, Z=4 a=7.138 Å b=9.259 Å c=5.861 Å (stable phase)	Crystallo- graphic and thermal meas- urements	T <sub>t</sub> , 686 K (orthorhombic → hexagonal) II → I		[1, 2]											
	High pressure studies	Three new phases III, IV, and V appear at pressures up to 45 kbar	The triple points are given as follows: <table><tr><td></td><td>Pressure, kbar</td><td>Temperature, K</td></tr><tr><td>I/II/IV</td><td>11.3 ± 1</td><td>745 ± 5</td></tr><tr><td>II/III/IV</td><td>14.6 ± 1</td><td>694 ± 7</td></tr><tr><td>I/IV/V</td><td>20.4 ± 1</td><td>809 ± 7</td></tr></table>		Pressure, kbar	Temperature, K	I/II/IV	11.3 ± 1	745 ± 5	II/III/IV	14.6 ± 1	694 ± 7	I/IV/V	20.4 ± 1	809 ± 7
	Pressure, kbar	Temperature, K													
I/II/IV	11.3 ± 1	745 ± 5													
II/III/IV	14.6 ± 1	694 ± 7													
I/IV/V	20.4 ± 1	809 ± 7													
<i>Potassium chromate</i> K <sub>2</sub> CrO <sub>4</sub> , orthorhombic space group, Pnam Z=4 a=7.61 Å b=10.40 Å c=5.92 Å (stable phase)	Crystallo- graphic and thermal measurements	T <sub>t</sub> , 952 K	The transformation is accom- panied by change in color from yellow to red.	[1, 4]											
	Thermal analysis	T <sub>t</sub> , 939 K (α → β)	Color change is attributed to some gradual change in β— K <sub>2</sub> CrO <sub>4</sub> and not due to poly- morphic transformation. β— K <sub>2</sub> CrO <sub>4</sub> is hexagonal with a= 6.125 Å c=8.245 Å at 978 K.	[1, 5–7]											



## 6. The Chromates – Continued

Substance	Measurement technique	Observations	Remarks	References
	Specific heat between 80 and 300 K	No transformation		[8]
	Magnetic susceptibility (89–723 K)	$\chi$ is independent of temperature.		[9]
	Dielectric permittivity and loss	From the behaviour of $\epsilon'$ and $\epsilon''$ , the development of the transformation process in time can be followed and transition rate can be determined.	The effect of different variables on the polymorphic transformation can also be determined.	[10]
	High pressure studies	No indication of polymorphism in the temperature range 293–473 K up to 12 kbar, but there appear three new high pressure polymorphs of $K_2CrO_4$ between 20 and 100 kbar. A triple point between the phases $\alpha$ , $\gamma$ , and $\delta$ is near 923 K at 28.5 kbar.		[11, 12]
<i>Strontium chromate</i> $SrCrO_4$ , monoclinic $P2_1/n-C_{2h}^5$ $Z=4$ $a=7.081 \text{ \AA}$ $b=7.388 \text{ \AA}$ $c=6.771 \text{ \AA}$ $\beta=103^\circ 25' \pm 5'$ (stable phase)	Crystallographic study	A possible orthorhombic high temperature phase at 1148 K, has been reported.		[13]
<i>Thallium chromate</i> $Tl_2CrO_4$ , Orthorhombic, $Pmcn$ $a=5.910 \text{ \AA}$ $b=10.727 \text{ \AA}$ $c=7.910 \text{ \AA}$ (stable phase)	Crystallographic, DTA and elec. conductivity studies	$T_t$ , 638 K, $\Delta H_{tr}$ , 15 cal mol <sup>-1</sup> (I) $T_k$ 795 K (774 K on cooling) (II) $\Delta H_{tr}$ , 70 cal mol <sup>-1</sup> The trend in variation of lattice constants also shows an anomaly in $Tl_2CrO_4$ between 523 and 623 K.	The second order phase transformation around 638 K was disputed by Sladky [12]. The high temperature hexagonal phase has cell dimensions: $a=10.04 \pm 0.04 \text{ \AA}$ $c=16.28 \pm 0.08 \text{ \AA}$ at 803 K.	[14–17]
<i>Lead chromate</i> $PbCrO_4$ , monoclinic space group: $P2_1/n-C_{2h}^5$ $Z=4$ $a=7.118 \pm 0.004 \text{ \AA}$ $b=7.434 \pm 0.004 \text{ \AA}$ $c=6.794 \pm 0.004 \text{ \AA}$ $\beta=102^\circ 25.5' \pm 2'$ (stable phase)	Crystallography and thermal analysis	$T_t$ , 980 K–1056 K	$PbCrO_4$ , however, has also been found to evolve oxygen around 873 K due to decomposition to $Pb_2CrO_5$ and $Cr_2O_3$ .	[13, 18–20]

## 6. The Chromates – Continued

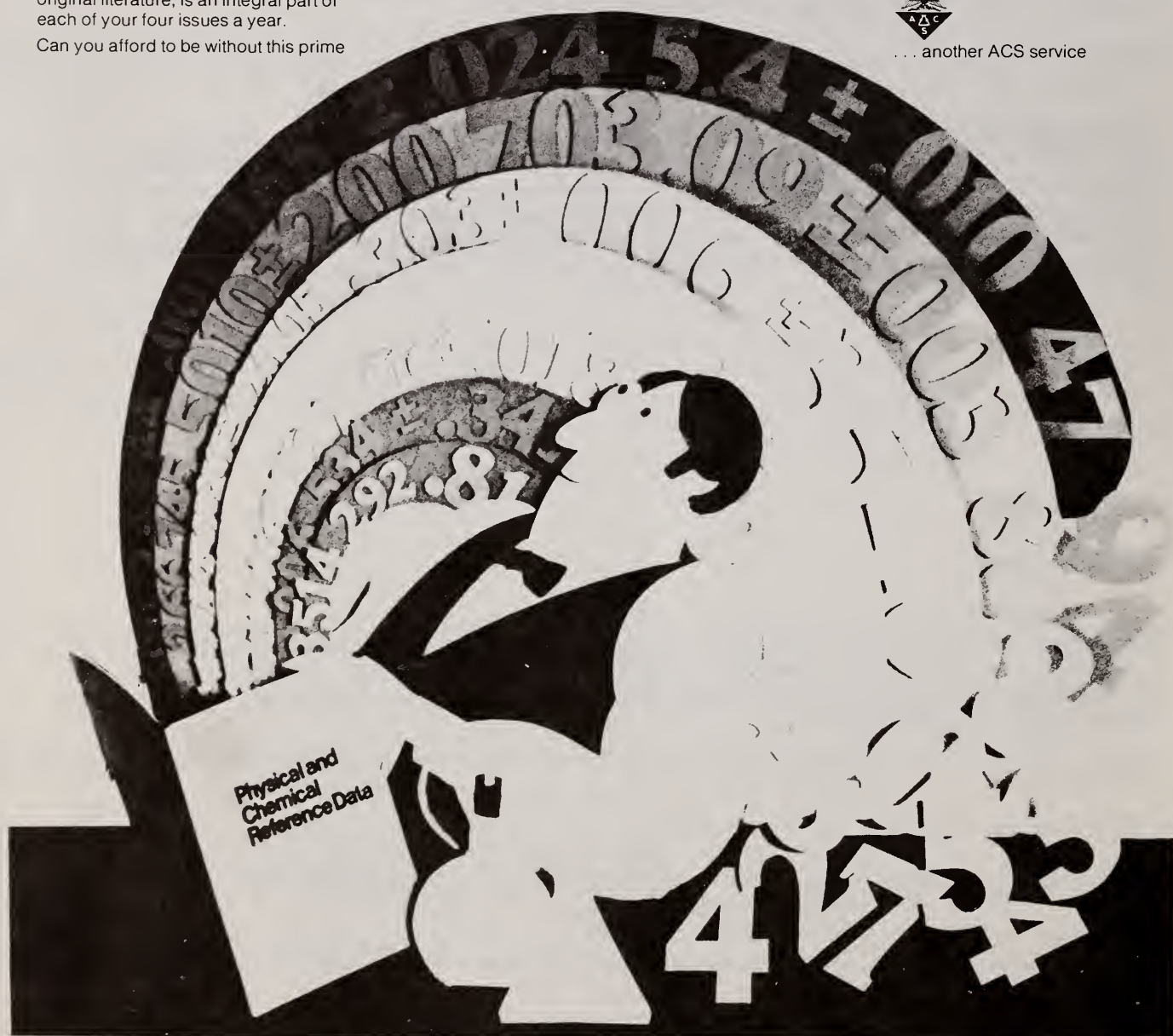
Substance	Measurement technique	Observations	Remarks	References
<i>Silver chromate</i> $\text{Ag}_2\text{CrO}_4$ , orthorhombic, space group: $\text{Pnma}$ $Z = 4$ $a = 10.063 \pm 0.011 \text{ \AA}$ $b = 7.029 \pm 0.004 \text{ \AA}$ $c = 5.540 \pm 0.002 \text{ \AA}$ (stable phase)	DTA and electrical conductivity	$T_i$ , 762–766 K orthorhombic $\rightarrow$ hexagonal (II) (I)	At lower temperatures $\text{Ag}_2\text{CrO}_4$ is an $n$ -type semiconductor, which transforms to a $p$ -type semiconductor at higher temperatures.	[21–23]
	High pressure studies	The II $\rightarrow$ I transition temperatures to 40 kbar were fitted as $t(^{\circ}\text{C}) = 479 + 2.3 P - 0.020 P^2$		[24]

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4. TITLE AND SUBTITLE  Crystal Structure Transformations in Inorganic Sulfates, Phosphates, Perchlorates, and Chromates			5. Publication Date November 1975	
			6. Performing Organization Code	
7. AUTHOR(S) C. N. R. Rao and B. Prakash			8. Performing Organ. Report No.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS  NATIONAL BUREAU OF STANDARDS DEPARTMENT OF COMMERCE WASHINGTON, D.C. 20234			10. Project/Task/Work Unit No.	
			11. Contract/Grant No.	
12. Sponsoring Organization Name and Complete Address (Street, City, State, ZIP) Same as No. 9 through the Special International Program (NBS-G-77)			13. Type of Report & Period Covered N/A	
			14. Sponsoring Agency Code	
15. SUPPLEMENTARY NOTES Library of Congress Catalog Card Number: 75-619082				
16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)  Literature dealing with crystal structure transformations of simple inorganic sulfates, phosphates, perchlorates and chromates has been critically reviewed. Data on thermodynamic, crystallographic, spectroscopic, dielectric and other properties are given. Experimental techniques employed to obtain the data are indicated and comments on the data are made wherever necessary. All pertinent references to the published literature (up to 1974) are listed.				
17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons) Chromates: crystal structure; crystal structure transformations; perchlorates; phase transformations; phosphates; sulfates; thermodynamic data; X-ray diffraction data.				
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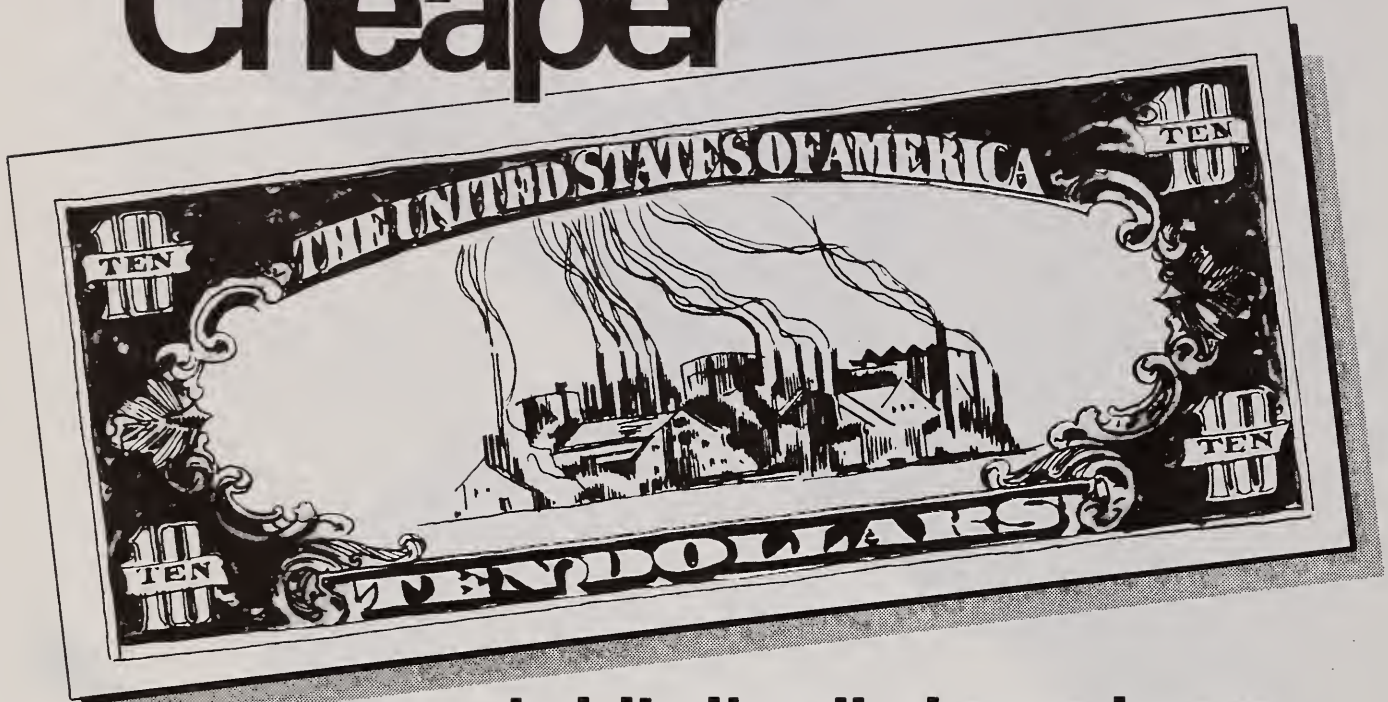


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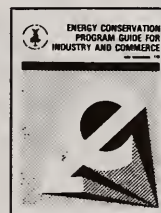
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