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Relaxation Modes of Trapped Crystal Point Defects: the Three-Neighbor Shells Model in NaCl

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The results of a relaxation-mode analysis are presented for two cases of trapped-defect relaxation in the NaCl structure, in which both defects occupy the same type of site (e.g., impurity divalent ion and trapped vacancy), or in which they occupy the two different types of sites (vacancy pair). The relaxation analysis is presented in the form of a set of basis vectors in occupation-probability space and a set of secular equations. Solutions to the equations provide the relaxation rates and also the coefficients in the linear combinations of the basis vectors which constitute the relaxation modes.

Calculations of the relaxation rates and contributions to the polarizability of the various modes for a three-shell model with jump frequencies chosen to represent the relaxation of an impurity-ion vacancy pair in NaCl(Mn) have confirmed the results of Lozovskii. Even though the third shell makes a significant and even large contribution to the process, one mode dominates and the relaxation as seen in a-c measurements would take place with essentially a single relaxation time. The d-c techniques of Dreyfus are sensitive enough to detect more than one of these relaxations at low temperatures, but the slowest of these will always be the dominant one. Any relaxation slower than the major one must be ascribed to some other mechanism.

1. Introduction

Point defects in crystals give rise to mechanical and elastic relaxation in a variety of ways. In particular, because of their interaction with each other, pairs of them can become mutually trapped, forming centers which can contribute to the response to applied mechanical or electrical stresses. If one defect is considered as the trap, then the trapped defect can occupy various lattice sites in the neighborhood of the trap. These accessible sites may be restricted to those in the nearest neighbor shell to the trap because of very strong interaction, or they may include sites in shells further away from the trap. Under the influence of the applied stress, some of the accessible sites become preferred over others that are equivalent in the stress free crystal, and the redistribution of the trapped defects according to the new scheme constitutes the relaxation process.

The rate equations governing this redistribution process constitute an eigenvalue problem, for which group representation theory combined with a knowledge of the symmetry around the trap provide a powerful tool for solution [1–3].[1] The results of this treatment are expressed in terms of relaxation modes, which represent certain distributions of the trapped defects among the accessible sites. Each of these distributions relaxes as a unit with the same exponential time function, exhibiting a single relaxation time, governing the occupation probability of all the sites.

Haven and van Santen [1, 2] applied the group theory technique to the case of cation vacancies trapped near divalent cation impurities in the NaCl structure, with only the nearest neighbor sites included. Wachtman [3] showed that the relaxation modes of the undriven

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[1] Figures in brackets indicate the literature references at the end of this paper.

situation were also solutions for the driven case in the limit of small applied stresses, and applied the technique to the relaxation of oxygen vacancies trapped at divalent cation impurities (Ca ions) in ThO_2, again restricting the vacancies to nearest neighbor sites. Bhagavantam and Pantulu [4] have summarized this approach for the case of nearest neighbor sites and have emphasized the similarity of the symmetry arguments to those arising in the treatment of infrared and Raman spectra. Franklin [5] showed that the technique could be extended to the case in which additional shells, further out than the nearest-neighbor shell, were accessible, and gave solutions for the case of cation vacancies trapped at divalent cation impurities in the NaCl structure, including two shells of accessible sites.

In considering the dielectric and mechanical behavior of these centers, the more distant shells of sites must, at least in principle, be included. It is expected that, at least beyond the first two shells, the binding energy of the sites will decrease with distance from the center, and the probability of occupation will fall off in the more distant sites. However, there are more sites available in the more distant shells. In the dielectric case, also, the more distant sites will make a larger contribution through their larger dipole moments, so that even a relatively small occupation probability could be important. The influence of the more distant shells is expected to be important when the differences in binding energies of the shells are not too large, and when the temperatures are high.

The experimental data are best defined in the case of dielectric relaxation in the alkali halides containing divalent impurities [6–10]. When care is taken to avoid precipitation of the divalent impurity, the frequency spectrum of the relaxation ascribable to these centers can be described as a typical Debye peak, with but a single relaxation time. Lidiard [11] has shown that this is to be expected if the first two shells of neighbors are included in the calculation, and reasonable values assigned to the probabilities for jumps of the vacancy between and within shells. Recently, Dreyfus [12], using a d-c technique of considerably greater time resolution than found in the usual a-c methods, was able to separate two distinct relaxations for which he could account using Lidiard's treatment, and another, slower, relaxation which he has tentatively ascribed to the third and more distant shells.

Lozovskii [13] has made a relaxation mode analysis for this dielectric relaxation including three shells of sites, but considering two rather special cases. For binding energies of the various shells, he chose (1) purely Coulombic values arising from the electrostatic interaction between point charges in a dielectric medium, and (2) the same value for all shells. He calculated both the relaxation times relative to the jump time in the first shell and the relative contributions to the polarizability from each mode. His results indicate that there should be four active modes, but that one will predominate, so that a close approximation to a Debye peak should result even when the third shell is included. Furthermore, the dominant relaxation in both cases was the slowest one. Dreyfus "fast" and "very fast" polarizations can be ascribed to the dominant mode and a superposition of the other three; but since the dominant mode should be the slowest, Lozovskii's result suggests that Dreyfus' "slow" polarization should not be ascribed to the outer shells.

In part 1 of the present paper, we extend the mode analysis to the third shell of neighbors for two cases in the NaCl structure. The Matched Point Defect Pair, in which the trap and the moving defect are both on lattice sites of one kind, as for a cation (anion) vacancy trapped near a cation (anion) impurity; and the Unmatched Point Defect Pair, in which the trap is on one kind of site and the moving defect is on the other, as in a vacancy pair, where either vacancy can be considered as the trapped and the other as the moving defect. This analysis includes all possible relaxation modes under all possible stresses, and includes a discussion of the determination of which modes are excited by a given applied stress. In part 2, we present calculations similar to those of Lozovskii for the relaxation times and polarizabilities for the dielectric relaxation of the three-shell model of a Matched Pair. These calculations have been made with a set of binding energies chosen to provide as realistic as possible a description of the situation in NaCl (Mn), and the results are compared to the available data.

2. Relaxation Modes of Pairs of Point Defects in the NaCl Structure

2.1. Matched Defect Pair (Impurity Ion—Vacancy)

This calculation is a straightforward extension of that reported previously [5] for the two-shell model. The modes for the three-shell model will be linear combinations of the previous ones together with new contributions from the third shell. Because of the complexity of the situation, with 42 sites available to the moving defect, it is preferable to report the modes in tabular form rather than graphically as done before. A 42-fold vector space is defined by the occupation probabilities of the accessible sites. Any distribution is then expressed as a vector $\vec{p}$ in this space. The rate equations are expressible in matrix form, involving a matrix $\mathbf{C}$ whose elements are c_{ij}, the negative probabilities per unit time that the moving defect will jump from the ith site to the jth site, and c_{ii}, the sum of all jump probabilities out of the ith site. The solutions to the rate equations are then expressible as sums of the eigenvectors of the matrix $\mathbf{C}$,

$$\vec{p}=\left[\vec{u}_1+\sum_{i=2}^{N} f_i\vec{u}_i\right]\left(\sum_{K} u_{1k}\right)^{-1}, \text{ where } f_i=f_{i0}\exp\left[-\lambda_i t\right].$$

In this equation, the $\vec{u}_i$ are the normalized eigenvectors of $\mathbf{C}$, $\vec{u}_1$ is the eigenvector for which the eigenvalue (jump rate) is zero and which represents the equilibrium distribution, and the u_{1k} are the components of $\vec{u}_1$. N is the total number of accessible sites, the λ_i are the eigenvalues (jump rates, or reciprocal relaxation times), and the f_{i0} are determined by the initial distribution.

In the irreducible representation technique, the eigenvectors $\vec{u}_i$ are expressed in terms of a set of normalized basis vectors $\vec{v}_{ij}$. To each irreducible representation of the point group of the relaxing center in the vector space of site occupation probabilities corresponds a subspace, spanned by one set of these basis vectors, and from which an equal number of eigenvectors can be constructed. If a transformation matrix is constructed of all of these vectors as columns, it can then be used to transform the matrix $\mathbf{C}$ to reduced form. The problem has then been reduced to a set of secular equations, one for each irreducible representation whose solutions provide the eigenvalues and the coefficients in the linear combinations of the rectors $\vec{v}_{ij}$ that form the eigenvectors $\vec{u}_i$.

In table 2.1 below, we list the 42 basis vectors used for this problem. The first column numbers the 42 sites in the first three shells of neighbors, and the second column identifies their lattice position with respect to the impurity atom, relative to the cation-anion separation. In the succeeding columns are listed the vectors used as basis vectors, arranged by irreducible representations, which are identified at the top of the columns. As it stands, this table is also the transformation matrix, except that for convenience of presentation, the basis vectors have not been normalized. The irreducible representations are identified in the notation of Eyring, Walter, and Kimball [14].

The secular equations corresponding to each irreducible representation are presented next. It is understood that in solving these secular equations, the normalized basis vectors must be used. The w_{ij} are the probabilities per unit time that the vacancy in a site in the ith shell will jump into a neighboring one in the jth shell. Only jumps from a site to one of its 12 nearest neighbors are allowed. For the interchange of the impurity ion and a vacancy on a first shell site, w_i is used. Analytical solutions for the eigenvalues and for the coefficients in the linear combinations of the basis vectors to form the eigenvectors have not been obtained for the E_g, T_{1u} and the T_{2g} representations.

A_{1g}: $$\begin{bmatrix} A & -2\sqrt{2}w_{21} & -2\sqrt{2}w_{31} \\ -2\sqrt{2}w_{12} & B & -2w_{32} \\ -2\sqrt{2}w_{13} & -2w_{23} & C \end{bmatrix}\vec{u}=\lambda\vec{u}$$

TABLE 2.1. *Basis vectors (unnormalized) for the matched point defect pair in the NaCl structure*

Site	xyz	A_{1g}			A_{2u}	E_g						E_u		T_{1g}			T_{1u}												T_{2g}									T_{2u}					
1	$\bar{1}\bar{1}0$	1	----	----	----	-2	----	----	0	----	----	----	----	----	----	----	-1	----	----	----	-1	----	----	----	0	----	----	----	1	----	----	0	----	----	0	----	----	0	----	-1	----	1	----
2	$0\bar{1}1$	1	----	----	----	1	----	----	-1	----	----	----	----	----	----	----	0	----	----	----	-1	----	----	----	1	----	----	----	0	----	----	-1	----	----	0	----	----	-1	----	0	----	-1	----
3	$1\bar{1}0$	1	----	----	----	-2	----	----	0	----	----	----	----	----	----	----	1	----	----	----	-1	----	----	----	0	----	----	----	-1	----	----	0	----	----	0	----	----	0	----	1	----	1	----
4	$0\bar{1}\bar{1}$	1	----	----	----	1	----	----	-1	----	----	----	----	----	----	----	0	----	----	----	-1	----	----	----	-1	----	----	----	0	----	----	1	----	----	0	----	----	1	----	0	----	-1	----
5	$\bar{1}01$	1	----	----	----	1	----	----	1	----	----	----	----	----	----	----	-1	----	----	----	0	----	----	----	1	----	----	----	0	----	----	0	----	----	-1	----	----	1	----	1	----	0	----
6	101	1	----	----	----	1	----	----	1	----	----	----	----	----	----	----	1	----	----	----	0	----	----	----	1	----	----	----	0	----	----	0	----	----	1	----	----	1	----	-1	----	0	----
7	$10\bar{1}$	1	----	----	----	1	----	----	1	----	----	----	----	----	----	----	1	----	----	----	0	----	----	----	-1	----	----	----	0	----	----	0	----	----	-1	----	----	-1	----	-1	----	0	----
8	$\bar{1}0\bar{1}$	1	----	----	----	1	----	----	1	----	----	----	----	----	----	----	-1	----	----	----	0	----	----	----	-1	----	----	----	0	----	----	0	----	----	1	----	----	-1	----	1	----	0	----
9	$\bar{1}10$	1	----	----	----	-2	----	----	0	----	----	----	----	----	----	----	-1	----	----	----	1	----	----	----	0	----	----	----	-1	----	----	0	----	----	0	----	----	0	----	-1	----	-1	----
10	011	1	----	----	----	1	----	----	-1	----	----	----	----	----	----	----	0	----	----	----	1	----	----	----	1	----	----	----	0	----	----	1	----	----	0	----	----	-1	----	0	----	1	----
11	110	1	----	----	----	-2	----	----	0	----	----	----	----	----	----	----	1	----	----	----	1	----	----	----	0	----	----	----	1	----	----	0	----	----	0	----	----	0	----	1	----	-1	----
12	$01\bar{1}$	1	----	----	----	1	----	----	-1	----	----	----	----	----	----	----	0	----	----	----	1	----	----	----	-1	----	----	----	0	----	----	-1	----	----	0	----	----	1	----	0	----	1	----
13	$\bar{2}00$	----	1	----	----	----	-1	----	----	1	----	----	----	----	----	----	----	-1	----	----	----	0	----	----	----	0	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----
14	002	----	1	----	----	----	2	----	----	0	----	----	----	----	----	----	----	0	----	----	----	0	----	----	----	1	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----
15	200	----	1	----	----	----	-1	----	----	1	----	----	----	----	----	----	----	1	----	----	----	0	----	----	----	0	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----
16	$00\bar{2}$	----	1	----	----	----	2	----	----	0	----	----	----	----	----	----	----	0	----	----	----	0	----	----	----	-1	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----
17	$0\bar{2}0$	----	1	----	----	----	-1	----	----	-1	----	----	----	----	----	----	----	0	----	----	----	-1	----	----	----	0	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----
18	020	----	1	----	----	----	-1	----	----	-1	----	----	----	----	----	----	----	0	----	----	----	1	----	----	----	0	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----
19	$\bar{2}\bar{1}1$	----	----	1	1	----	----	-1	----	----	1	-1	1	1	-1	0	----	----	-1	0	----	----	0	-1	----	----	0	1	----	0	1	----	-1	0	----	0	-1	----	1	----	0	----	1
20	$\bar{1}\bar{1}2$	----	----	1	1	----	----	2	----	----	0	2	0	0	1	1	----	----	0	-1	----	----	0	-1	----	----	1	0	----	1	0	----	0	-1	----	0	-1	----	0	----	1	----	-1
21	$\bar{1}\bar{2}1$	----	----	1	1	----	----	-1	----	----	-1	-1	-1	-1	0	-1	----	----	0	-1	----	----	-1	0	----	----	0	1	----	0	1	----	0	-1	----	-1	0	----	-1	----	-1	----	0
22	$\bar{2}11$	----	----	1	-1	----	----	-1	----	----	1	1	-1	-1	-1	0	----	----	-1	0	----	----	0	1	----	----	0	1	----	0	-1	----	1	0	----	0	-1	----	1	----	0	----	-1
23	$\bar{1}21$	----	----	1	-1	----	----	-1	----	----	-1	1	1	1	0	1	----	----	0	-1	----	----	1	0	----	----	0	1	----	0	-1	----	0	1	----	-1	0	----	-1	----	-1	----	0
24	$\bar{1}12$	----	----	1	-1	----	----	2	----	----	0	-2	0	0	1	-1	----	----	0	-1	----	----	0	1	----	----	1	0	----	-1	0	----	0	1	----	0	-1	----	0	----	1	----	1
25	121	----	----	1	1	----	----	-1	----	----	-1	-1	-1	-1	0	1	----	----	0	1	----	----	1	0	----	----	0	1	----	0	1	----	0	1	----	1	0	----	-1	----	1	----	0
26	211	----	----	1	1	----	----	-1	----	----	1	-1	1	1	1	0	----	----	1	0	----	----	0	1	----	----	0	1	----	0	1	----	1	0	----	0	1	----	1	----	0	----	-1
27	112	----	----	1	1	----	----	2	----	----	0	2	0	0	-1	-1	----	----	0	1	----	----	0	1	----	----	1	0	----	1	0	----	0	1	----	0	1	----	0	----	-1	----	1
28	$1\bar{2}1$	----	----	1	-1	----	----	-1	----	----	-1	1	1	1	0	-1	----	----	0	1	----	----	-1	0	----	----	0	1	----	0	-1	----	0	-1	----	1	0	----	-1	----	1	----	0
29	$2\bar{1}1$	----	----	1	-1	----	----	-1	----	----	1	1	-1	-1	1	0	----	----	1	0	----	----	0	-1	----	----	0	1	----	0	-1	----	-1	0	----	0	1	----	1	----	0	----	1
30	$1\bar{1}2$	----	----	1	-1	----	----	2	----	----	0	-2	0	0	-1	1	----	----	0	1	----	----	0	-1	----	----	1	0	----	-1	0	----	0	-1	----	0	1	----	0	----	-1	----	-1
31	$\bar{1}\bar{2}\bar{1}$	----	----	1	-1	----	----	-1	----	----	-1	1	1	-1	0	1	----	----	0	-1	----	----	-1	0	----	----	0	-1	----	0	1	----	0	1	----	1	0	----	1	----	-1	----	0
32	$\bar{1}\bar{1}\bar{2}$	----	----	1	-1	----	----	2	----	----	0	-2	0	0	-1	-1	----	----	0	-1	----	----	0	-1	----	----	-1	0	----	1	0	----	0	1	----	0	1	----	0	----	1	----	-1
33	$\bar{2}\bar{1}\bar{1}$	----	----	1	-1	----	----	-1	----	----	1	1	-1	1	1	0	----	----	-1	0	----	----	0	-1	----	----	0	-1	----	0	1	----	1	0	----	0	1	----	-1	----	0	----	1
34	$\bar{2}1\bar{1}$	----	----	1	1	----	----	-1	----	----	1	-1	1	-1	1	0	----	----	-1	0	----	----	0	1	----	----	0	-1	----	0	-1	----	-1	0	----	0	1	----	-1	----	0	----	-1
35	$\bar{1}1\bar{2}$	----	----	1	1	----	----	2	----	----	0	2	0	0	-1	1	----	----	0	-1	----	----	0	1	----	----	-1	0	----	-1	0	----	0	-1	----	0	1	----	0	----	1	----	1
36	$\bar{1}2\bar{1}$	----	----	1	1	----	----	-1	----	----	-1	-1	-1	1	0	-1	----	----	0	-1	----	----	1	0	----	----	0	-1	----	0	-1	----	0	-1	----	1	0	----	1	----	-1	----	0
37	$21\bar{1}$	----	----	1	-1	----	----	-1	----	----	1	1	-1	1	-1	0	----	----	1	0	----	----	0	1	----	----	0	-1	----	0	1	----	-1	0	----	0	-1	----	-1	----	0	----	-1
38	$11\bar{2}$	----	----	1	-1	----	----	2	----	----	0	-2	0	0	1	1	----	----	0	1	----	----	0	1	----	----	-1	0	----	1	0	----	0	-1	----	0	-1	----	0	----	-1	----	1
39	$12\bar{1}$	----	----	1	-1	----	----	-1	----	----	-1	1	1	-1	0	-1	----	----	0	1	----	----	1	0	----	----	0	-1	----	0	1	----	0	-1	----	-1	0	----	1	----	1	----	0
40	$2\bar{1}\bar{1}$	----	----	1	1	----	----	-1	----	----	1	-1	1	-1	-1	0	----	----	1	0	----	----	0	-1	----	----	0	-1	----	0	-1	----	1	0	----	0	-1	----	-1	----	0	----	1
41	$1\bar{1}\bar{2}$	----	----	1	1	----	----	2	----	----	0	2	0	0	1	-1	----	----	0	1	----	----	0	-1	----	----	-1	0	----	-1	0	----	0	1	----	0	-1	----	0	----	-1	----	-1
42	$1\bar{2}\bar{1}$	----	----	1	1	----	----	-1	----	----	-1	-1	-1	1	0	1	----	----	0	1	----	----	-1	0	----	----	0	-1	----	0	-1	----	0	1	----	-1	0	----	1	----	1	----	0
Vector No.		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42

where

$$A=2w_{12}+4w_{13}$$

$$B=4w_{21}+4w_{23}$$

$$C=2w_{31}+w_{32}.$$

Solutions for λ are

$$\lambda=0,\ 1/2\{(A+B+C)\pm[(B-C+2w_{12}-4w_{13})^2+16(w_{13}-w_{23})(2w_{12}-w_{32})]^{1/2}\}$$

$$\vec{u}=a\vec{v}_1+b\vec{v}_2+c\vec{v}_3.$$

(The vectors $\vec{v}_1$, etc., are given in table 2.1.)

. . . .

A_{2u}:

$$\lambda=C$$

$$\vec{u}=\vec{v}_4$$

. . . .

E_g:

$$\begin{pmatrix} D & -\sqrt{2}w_{21} & -\sqrt{2}w_{31} \\ -\sqrt{2}w_{12} & B & -2w_{32} \\ -\sqrt{2}w_{13} & -2w_{23} & E \end{pmatrix}\vec{u}=\lambda\vec{u}$$

where

$$D=2w_{12}+4w_{13}+6w_{11}$$

$$E=2w_{31}+w_{32}+3w_{33}$$

$$\vec{u}=a\vec{v}_5+b\vec{v}_6+c\vec{v}_7$$

or

$$=a\vec{v}_8+b\vec{v}_9+c\vec{v}_{10}$$

. . . .

E_u:

$$\lambda=2w_{31}+w_{32}+3w_{33}$$

$$\vec{u}=\vec{v}_{11} \text{ or } \vec{v}_{12}$$

. . . .

T_{1g}:

$$\lambda=2w_{31}+w_{32}+3w_{33}$$

$$\vec{u}=\vec{v}_{13},\ \vec{v}_{14},\ \text{or } \vec{v}_{15}$$

. . . .

T_{1u}:

$$\begin{pmatrix} K & -2w_{21} & -2w_{31} & -\sqrt{2}w_{31} \\ -2w_{12} & B & -2w_{32} & 0 \\ -2w_{13} & -2w_{23} & G & -\sqrt{2}w_{33} \\ -\sqrt{2}w_{13} & 0 & -\sqrt{2}w_{33} & H \end{pmatrix}\vec{u}=\lambda\vec{u}$$

where

$$K=2w_{12}+4w_{13}+2w_{11}+2w_{i}$$

$$\vec{u}=a\vec{v}_{16}+b\vec{v}_{17}+c\vec{v}_{18}+d\vec{v}_{19}$$

or

$$=a\vec{v}_{20}+b\vec{v}_{21}+c\vec{v}_{22}+d\vec{v}_{23}$$

or

$$=a\vec{v}_{24}+b\vec{v}_{25}+c\vec{v}_{26}+d\vec{v}_{27}$$

. . . .

T_{2g}:

$$\begin{bmatrix} F & 0 & -2w_{31} \\ 0 & G & -\sqrt{2}w_{33} \\ -2w_{13} & -\sqrt{2}w_{33} & H \end{bmatrix}\vec{u}=\lambda\vec{u}$$

where

$$F=2w_{12}+4w_{13}+4w_{11}$$

$$G=2w_{31}+w_{32}+2w_{33}$$

$$H=2w_{31}+w_{32}+w_{33}$$

$$\vec{u}=a\vec{v}_{28}+b\vec{v}_{29}+c\vec{v}_{30}$$

or

$$=a\vec{v}_{31}+b\vec{v}_{32}+c\vec{v}_{33}$$

or

$$=a\vec{v}_{34}+b\vec{v}_{35}+c\vec{v}_{36}$$

. . . .

T_{2u}:

$$\begin{pmatrix} J & -\sqrt{2}w_{31} \\ -\sqrt{2}w_{13} & E \end{pmatrix}\vec{u}=\lambda\vec{u}$$

where $J=2w_{12}+4w_{13}+6w_{11}+2w_{i}$.

Solutions for λ are: $\lambda=1/2\,\{(J+E)\pm[(J-E)^2+8w_{13}w_{31}]^{1/2}\}$

$$\vec{u}=a\vec{v}_{37}+b\vec{v}_{38}$$

or

$$=a\vec{v}_{39}+b\vec{v}_{40}$$

or

$$=a\vec{v}_{41}+b\vec{v}_{42}$$

. . . .

2.2. Unmatched Point Defect Pair (Vacancy Pair)

The method of calculation is similar to that for the matched point defect pair. Each configuration can be changed into another accessible one by jump of either the cation or the anion defect. Hence, the jump probabilities always occur as the sum of that for the cation and that for the anion defect, and in the notation used here, only these sums will be used. It should also be noted that there are two different types of jumps from a site in the third shell to another in the same shell, distinguished by the path taken. For example, the sites in the third shell are designated by (2,1,0) and its permutations, including negative signs. A jump can only be made to another site in this shell for which the x,y,z differ by ± 1. If the zero stays fixed, there is only one such jump, and the defect remains in a (100) plane as it moves. During the jump, it is screened from the other defect by an ion of opposite sign, in the same (100) plane. The other two possible jumps are with the two remaining fixed, for which the path is not screened. Presumably, the activation energies for these two jumps will not be the same, and so they will have different jump probabilities. These will be designated by w'_{33} for the screened and w''_{33} for the unscreened jump. With these changes, the notation as used for the previous example will be used to designate the jump probabilities.

The basis vectors are given in table 2.2, again using the cation-anion separation lattice parameter as the repeat distance in designating the sites. The secular equations are given below from which the eigenvalues and coefficients in the linear combinations of basis vectors constituting the eigenvectors can be derived as before.

A_{1g}:

$$\begin{bmatrix} A' & -2\sqrt{3}w_{21} & -2w_{31} \\ -2\sqrt{3}w_{12} & B' & -2\sqrt{3}w_{32} \\ -2w_{13} & -2\sqrt{3}w_{23} & C' \end{bmatrix} \vec{u}=\lambda\vec{u}$$

where

$$A'=4w_{12}+4w_{13}$$

$$B'=3w_{21}+6w_{23}$$

$$C'=w_{31}+2w_{32}.$$

Solutions for λ are

$$\lambda=0,\ 1/2\{(A'+B'+C')\pm[(B'-C'+4w_{12}-4w_{13})^2+16(2w_{13}-3w_{23})(2w_{12}-w_{32})]^{1/2}\}$$

$$\vec{u}=a\vec{v}_1+b\vec{v}_2+c\vec{v}_3.$$

(The vectors $\vec{v}_1$, etc., are given in table 2.2.)

……

A_{2g}:

$$\lambda=w_{31}+2w_{32}+2w'_{33}+4w''_{33}$$

$$\vec{u}=\vec{v}_4$$

……

A_{2u}:

$$\lambda=3w_{21}+6w_{23}$$

$$\vec{u}=\vec{v}_5$$

……

E_g:

$$\begin{bmatrix} D' & -\sqrt{3}w_{31} & -w_{31} \\ -\sqrt{3}w_{13} & E' & -\sqrt{3}w''_{33} \\ -w_{13} & -\sqrt{3}w''_{33} & E'' \end{bmatrix} \vec{u}=\lambda\vec{u}$$

where

$$D'=4w_{12}+4w_{13}+6w_{11}$$

$$E'=w_{31}+2w_{32}+2w'_{33}+w''_{33}$$

$$E''=w_{31}+2w_{32}+3w''_{33}$$

$$\vec{u}=a\vec{v}_6+b\vec{v}_7+c\vec{v}_8$$

$$=a\vec{v}_9+b\vec{v}_{10}+c\vec{v}_{11}$$

……

TABLE 2.2. *Basis vectors (unnormalized) for the unmatched point defect pair in the NaCl structure*

Site	*xyz*	A_{1g}			A_{2g}	A_{2u}	E_g						T_{1g}			T_{1u}												T_{2g}						T_{2u}					
1	100	1	----	----	----	----	−1	----	----	1	----	----	----	----	----	1	----	----	----	0	----	----	----	0	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----
2	$\bar{1}00$	1	----	----	----	----	−1	----	----	1	----	----	----	----	----	−1	----	----	----	0	----	----	----	0	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----
3	010	1	----	----	----	----	−1	----	----	−1	----	----	----	----	----	0	----	----	----	1	----	----	----	0	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----
4	$0\bar{1}0$	1	----	----	----	----	−1	----	----	−1	----	----	----	----	----	0	----	----	----	−1	----	----	----	0	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----
5	001	1	----	----	----	----	2	----	----	0	----	----	----	----	----	0	----	----	----	0	----	----	----	1	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----
6	$00\bar{1}$	1	----	----	----	----	2	----	----	0	----	----	----	----	----	0	----	----	----	0	----	----	----	−1	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----
7	111	----	1	----	----	1	----	----	----	----	----	----	----	----	----	----	1	----	----	----	1	----	----	----	1	----	----	1	----	1	----	1	----	----	----	----	----	----	----
8	$\bar{1}\bar{1}\bar{1}$	----	1	----	----	−1	----	----	----	----	----	----	----	----	----	----	−1	----	----	----	−1	----	----	----	−1	----	----	1	----	1	----	1	----	----	----	----	----	----	----
9	$\bar{1}\bar{1}1$	----	1	----	----	1	----	----	----	----	----	----	----	----	----	----	−1	----	----	----	−1	----	----	----	1	----	----	1	----	−1	----	−1	----	----	----	----	----	----	----
10	$11\bar{1}$	----	1	----	----	−1	----	----	----	----	----	----	----	----	----	----	1	----	----	----	1	----	----	----	−1	----	----	1	----	−1	----	−1	----	----	----	----	----	----	----
11	$\bar{1}1\bar{1}$		1	----	----	1	----	----	----	----	----	----	----	----	----	----	−1	----	----	----	1	----	----	----	−1	----	----	−1	----	−1	----	1	----	----	----	----	----	----	----
12	$1\bar{1}1$	----	1	----	----	−1	----	----	----	----	----	----	----	----	----	----	1	----	----	----	−1	----	----	----	1	----	----	−1	----	−1	----	1	----	----	----	----	----	----	----
13	$1\bar{1}\bar{1}$	----	1	----	----	1	----	----	----	----	----	----	----	----	----	----	1	----	----	----	−1	----	----	----	−1	----	----	−1	----	1	----	−1	----	----	----	----	----	----	----
14	$\bar{1}11$	----	1	----	----	−1	----	----	----	----	----	----	----	----	----	----	−1	----	----	----	1	----	----	----	1	----	----	−1	----	1	----	−1	----	----	----	----	----	----	----
15	210	----	----	1	1	----	----	0	2	----	−2	0	1	0	0	----	----	−1	2	----	----	2	1	----	----	0	0	----	1	----	0	----	0	0	0	1	2	−2	1
16	$1\bar{2}0$	----	----	1	−1	----	----	0	2	----	2	0	1	0	0	----	----	2	1	----	----	1	−2	----	----	0	0	----	−1	----	0	----	0	0	0	2	−1	1	2
17	$\bar{2}\bar{1}0$	----	----	1	1	----	----	0	2	----	−2	0	1	0	0	----	----	1	−2	----	----	−2	−1	----	----	0	0	----	1	----	0	----	0	0	0	−1	−2	2	−1
18	$\bar{1}20$	----	----	1	−1	----	----	0	2	----	2	0	1	0	0	----	----	−2	−1	----	----	−1	2	----	----	0	0	----	−1	----	0	----	0	0	0	−2	1	−1	−2
19	120	----	----	1	−1	----	----	0	2	----	2	0	−1	0	0	----	----	2	1	----	----	−1	2	----	----	0	0	----	1	----	0	----	0	0	0	2	−1	−1	−2
20	$2\bar{1}0$	----	----	1	1	----	----	0	2	----	−2	0	−1	0	0	----	----	−1	2	----	----	−2	−1	----	----	0	0	----	−1	----	0	----	0	0	0	1	2	2	−1
21	$\bar{1}\bar{2}0$	----	----	1	−1	----	----	0	2	----	2	0	−1	0	0	----	----	−2	−1	----	----	1	−2	----	----	0	0	----	1	----	0	----	0	0	0	−2	1	1	2
22	$\bar{2}10$	----	----	1	1	----	----	0	2	----	−2	0	−1	0	0	----	----	1	−2	----	----	2	1	----	----	0	0	----	−1	----	0	----	0	0	0	−1	−2	−2	1
23	021	----	----	1	1	----	----	1	−1	----	1	1	0	1	0	----	----	0	0	----	----	−1	2	----	----	2	1	----	0	----	1	----	0	−2	1	0	0	1	2
24	$01\bar{2}$	----	----	1	−1	----	----	−1	−1	----	−1	1	0	1	0	----	----	0	0	----	----	2	1	----	----	1	−2	----	0	----	−1	----	0	1	2	0	0	2	−1
25	$0\bar{2}\bar{1}$	----	----	1	1	----	----	1	−1	----	1	1	0	1	0	----	----	0	0	----	----	1	−2	----	----	−2	−1	----	0	----	1	----	0	2	−1	0	0	−1	−2
26	$0\bar{1}2$	----	----	1	−1	----	----	−1	−1	----	−1	1	0	1	0	----	----	0	0	----	----	−2	−1	----	----	−1	2	----	0	----	−1	----	0	−1	−2	0	0	−2	1
27	012	----	----	1	−1	----	----	−1	−1	----	−1	1	0	−1	0	----	----	0	0	----	----	2	1	----	----	−1	2	----	0	----	1	----	0	−1	−2	0	0	2	−1
28	$02\bar{1}$	----	----	1	1	----	----	1	−1	----	1	1	0	−1	0	----	----	0	0	----	----	−1	2	----	----	−2	−1	----	0	----	−1	----	0	2	−1	0	0	1	2
29	$0\bar{1}\bar{2}$	----	----	1	−1	----	----	−1	−1	----	−1	1	0	−1	0	----	----	0	0	----	----	−2	−1	----	----	1	−2	----	0	----	1	----	0	1	2	0	0	−2	1
30	$0\bar{2}1$	----	----	1	1	----	----	1	−1	----	1	1	0	−1	0	----	----	0	0	----	----	1	−2	----	----	2	1	----	0	----	−1	----	0	−2	1	0	0	−1	−2
31	102	----	----	1	1	----	----	−1	−1	----	1	−1	0	0	1	----	----	2	1	----	----	0	0	----	----	−1	2	----	0	----	0	----	1	1	2	−2	1	0	0
32	$\bar{2}01$	----	----	1	−1	----	----	1	−1	----	−1	−1	0	0	1	----	----	1	−2	----	----	0	0	----	----	2	1	----	0	----	0	----	−1	2	−1	1	2	0	0
33	$\bar{1}0\bar{2}$	----	----	1	1	----	----	−1	−1	----	1	−1	0	0	1	----	----	−2	−1	----	----	0	0	----	----	1	−2	----	0	----	0	----	1	−1	−2	2	−1	0	0
34	$20\bar{1}$	----	----	1	−1	----	----	1	−1	----	−1	−1	0	0	1	----	----	−1	2	----	----	0	0	----	----	−2	−1	----	0	----	0	----	−1	−2	1	−1	−2	0	0
35	201	----	----	1	−1	----	----	1	−1	----	−1	−1	0	0	−1	----	----	−1	2	----	----	0	0	----	----	2	1	----	0	----	0	----	1	2	−1	−1	−2	0	0
36	$\bar{1}02$	----	----	1	1	--	----	−1	−1	----	1	−1	0	0	−1	----	----	−2	−1	----	----	0	0	----	----	−1	2	----	0	--	0	----	−1	1	2	2	−1	0	0
37	$\bar{2}0\bar{1}$	----	----	1	−1,	----	----	1	−1	----	−1	−1	0	0	−1	----	----	1	−2	----	----	0	0	----	----	−2	−1	----	0	----	0	----	1	−2	1	1	2	0	0
38	$10\bar{2}$	----	----	1	1	----	----	−1	−1	----	1	−1	0	0	−1	----	----	2	1	----	----	0	0	----	----	1	−2	----	0	----	0	----	−1	−1	−2	−2	1	0	0
Vector No.		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38

T_{1g}:

$$\lambda = w_{31} + 2w_{32} + 2w'_{33} + 2w''_{33}$$

$$\vec{u} = \vec{v}_{12},\ \vec{v}_{13},\text{ or }\vec{v}_{14}$$

. . . .

T_{1u}:

$$\begin{bmatrix} K' & -2w_{21} & 2w_{31}/\sqrt{5} & -4w_{31}/\sqrt{5} \\ -2w_{12} & B' & -2w_{32}/\sqrt{5} & -6w_{32}/\sqrt{5} \\ 2w_{13}/\sqrt{5} & -2w_{23}/\sqrt{5} & L' & -(4w''_{33} - 3w'_{33})/5 \\ -4w_{13}/\sqrt{5} & -6w_{23}/\sqrt{5} & -(4w''_{33} - 3w'_{33})/5 & L'' \end{bmatrix} \vec{u} = \lambda \vec{u}$$

where

$$K' = 4w_{12} + 4w_{13} + 4w_{11}$$

$$L' = w_{31} + 2w_{32} + (9/5)w'_{33} + (8/5)w''_{33}$$

$$L'' = w_{31} + 2w_{32} + (1/5)w'_{33} + (2/5)w''_{33}$$

$$\vec{u} = av_{15} + b\vec{v}_{16} + c\vec{v}_{17} + d\vec{v}_{18}$$

or

$$= a\vec{v}_{19} + b\vec{v}_{20} + c\vec{v}_{21} + d\vec{v}_{22}$$

or

$$= a\vec{v}_{23} + b\vec{v}_{24} + c\vec{v}_{25} + d\vec{v}_{26}$$

. . . .

T_{2g}:

$$\begin{pmatrix} B' & -2w_{32} \\ -2w_{23} & G' \end{pmatrix} \vec{u} = \lambda \vec{u}$$

where

$$G' = w_{31} + 2w_{32} + 2w''_{33}.$$

Solutions for λ are $\lambda = 1/2\{(B' + G') \pm [(B' - G')^2 + 16w_{23}w_{32}]^{1/2}\}$

$$\vec{u} = a\vec{v}_{27} + b\vec{v}_{28}$$

$$= a\vec{v}_{29} + b\vec{v}_{30}$$

or

$$= a\vec{v}_{31} + b\vec{v}_{32}$$

. . . .

T_{2u}:

$$\begin{pmatrix} J' & (4w''_{33} - 3w''_{33})/5 \\ (4w''_{33} - 3w'_{33})/5 & J'' \end{pmatrix} \vec{u} = \lambda \vec{u}$$

where

$$J' = w_{31} + 2w_{32} + (1/5)w'_{33} + (12/5)w''_{33}$$

$$J'' = w_{31} + 2w_{32} + (9/5)w'_{33} + (18/)w''_{33}.$$

Solutions for λ are $\lambda = (w_{31} + 2w_{32} + w'_{33} + 3w''_{33}) \pm [w'^{2}_{33} + w''^{2}_{33}]^{1/2}$

$$\vec{u} = a\vec{v}_{33} + b\vec{v}_{34}$$

or

$$= a\vec{v}_{35} + b\vec{v}_{36}$$

or

$$= a\vec{v}_{37} + b\vec{v}_{38}$$

. . . .

2.3. Excitation of the Modes by Applied Stresses

While the analysis above reveals the modes by which a relaxation process can take place it does not provide any way of deciding which modes will be excited by a given applied stress. This question can, however, be answered in the following way. Consider the system under a constant stress of the specified sort. The influence of the stress will be to lower the symmetry of the crystal to that common to the applied stress and the undisturbed crystal (Curie's law [15]). Thus, from a knowledge of the symmetry of the applied stress and the undisturbed point group of the defect center under consideration, the point group under stress can be determined. It will be a subgroup of the unstressed point group. In the presence of the stress, the system will adopt the equilibrium configuration appropriate to the new point group, and represented by the new A_{1g} mode, for which the relaxation rate is zero. When the stress is removed, the system will begin to relax, but now with the modes appropriate to the undisturbed point group. Hence, the problem of deciding which modes will be excited is the problem of expressing the equilibrium mode under the stressed point group in terms of the unstressed modes.

The irreducible representations of the unstressed group each correspond to a subspace of the total vector space, such that these subspaces are mutually orthogonal. Under the stressed group, the equilibrium mode corresponds to a single vector, which must of necessity be a linear combination of mutually orthogonal components drawn from the appropriate subspaces identified with the irreducible representations of the unstressed group. Since each of these components, in turn, can be expressed as a linear combination of the basis vectors of the corresponding unstressed irreducible representation, then the stressed equilibrium mode must be expressible as a linear combination of the unstressed modes whose corresponding irreducible representations have as a component the stressed irreducible representation A_{1g}. Hence, the problem is to examine the irreducible representations of the unstressed group and determine which of these has as a component the stressed A_{1g} irreducible representation.

This determination is readily done with the character table. Since the irreducible representations of a group are also representations, although not necessarily irreducible, of its subgroups, the character table of the irreducible representations of the full group can be consulted, and the examination restricted to the entries under the elements of the subgroup. For a given irreducible representation of the full group, these constitute the characters of that representation of the subgroup, and by inspection and comparison to the character table for the subgroup, the components among the irreducible representations of the subgroup determined. In this way, all of the irreducible representations of the full group can be found that have as a component the A_{1g} representation of the subgroup. The corresponding relaxation modes of the unstressed system are those that will be excited by the stress that produced the subgroup.

As an example, consider the case of the matched point defect pair in NaCl, and let the stress be an electric field applied along one cube axis. The unstressed group is the full cubic group, m3m in the international notation; while under the field, this is reduced to 4mm. Inspection of the character tables reveals that the unstressed irreducible representations which have the A_1 irreducible representation of the stressed subgroup as a component are the A_{1g}, the E_g, and the T_{1u}. On the other hand, a simple tension or compression along a cube axis reduces the point group to 4/mmm, and results in excitation of the A_{1g} and the E_g. This result can be interpreted as follows. The A_{1g} mode will always be excited in principle, because a stress will never shift the distribution completely away from the equilibrium distribution, and there must be a term to describe what is left. The E_g mode represents the departure from equilibrium that provides the symmetric extension or contraction along the cube axis produced by the tension or compression. Under the axial electric field, this mode is also excited and corresponds to the electrostriction.

There is a rather simple way of determining the number of independent relaxation times to expect for the excited modes that parallels the above development. Under the applied stress, in the new point group, the sites will have been further subdivided into independent and noninteracting subspaces, analogous to the various shells of neighbors of the unstressed crystal.

The A_{1g} mode in the stressed point group will be the sum of vectors, one from each subspace, each formed simply by assigning unity to each site in the subspace. These vectors are the mutually orthogonal components making up the new equilibrium as discussed above. The number of distinct relaxation times observable in principle under the applied stress will be just the number of these independent subspaces produced with the proviso that one of these relaxation times will be infinite, corresponding to the equilibrium mode, and the others finite.

This treatment can, of course, be generalized. A listing of all subgroups reached by the application of any homogeneous second rank tensor stress to any crystal was given by Wachtman and Peiser [16]. In table 2.3, we complete this tabulation by listing all subgroups reached by the application of a vector stress, such as an electric field. Koptsik [17] has tabulated the subgroups reached by various types of influence, but his tables apparently do not apply to the present case. The subgroups which can be reached by application of an electric field have previously been listed by Vlokh and Zheludev, [18] but the meaning of their table for the cubic groups is hard to interpret, at least in the English translation. Table 2.3 also gives some additional information. The subgroups are classified as to whether they are normal subgroups (sometimes termed self-conjugate or invariant subgroups) of the starting point group. This classification shows that the cryptosymmetry theory of Niggli [19] and Wittke [20] apparently cannot be applied directly to the treatment of relaxation modes. In Niggli's theory, each atom is considered to have some additional property, such as magnetic moment, and the symmetry group possessed by the crystal when this additional property is taken into account must be a subgroup of the group obtained when this additional property is ignored. One might attempt to take the probability of occupation by a vacancy as the additional property and discuss relaxation modes in terms of cryptosymmetry. However, in Niggli's theory, only normal subgroups are permitted, and table 2.3 shows that many of the subgroups which can be reached by the action of an electric field are not normal subgroups. It thus appears that some modification or extension of the concept of cryptosymmetry would be required if it were applied to relaxation modes.

TABLE 2.3

Original point group	Vector field										Total number of symmetry subgroups other than original group	Number of subgroups other than original group reached by application of vector	Number of subgroups other than original group reached by application of symmetric tensor of second rank
	Subgroups												
	(C_{6v})	(C_6)	(C_{3v})	(C_3)	(C_{4v})	(C_4)	(C_{2v})	(C_s)	(C_2)	(C_1)			
	6mm	6	3m	3	4mm	4	mm2	m	2	1			
$m3m$ (O_h)			x—		x—		x—	x—		x	24	5	5
$\bar{4}3m$ (T_d)			x—				x—	x—		x	10	4	7
432 (0)				x—		x—			x—	x	8	4	5
$m3$ (T_h)				x—			x—	x—		x	11	4	4
23 (T)				x—					x—	x	4	3	4
$6/mmm$ (D_{6h})	x						x—	x		x	19	4	3
$6m2$ (D_{3h})			x				x—	x		x	8	4	4
$6mm$ (C_{6v})	0							x—		x	7	2	3
622 (D_6)		x							x	x	6	3	3
$6/m$ (C_{6h})		x						x		x	9	3	2
$\bar{6}$ (C_{3h})*				x				x		x	3	3	2
6 (C_6)*		0								x	3	1	2
$\bar{3}m$ (D_{3d})			x					x—	x—	x	9	4	2
$3m$ (C_{3v})			0					x—		x	3	2	2
32 (D_3)				x					x—	x	3	3	2
$\bar{3}$ (C_{3i})*				x						x	3	2	1
3 (C_3)*				0						x	1	1	1
$4/mmm$ (D_{4h})					x		x	x		x	14	4	3
$\bar{4}2m$ (D_{2d})							x	x—	x	x	6	4	5
$4mm$ (C_{4v})					0			x—		x	5	2	4
422 (D_4)						x			x	x	4	3	3
$4/m$ (C_{4h})						x		x		x	7	3	2
$\bar{4}$ (S_4)*									x	x	2	2	2
4 (C_4)*						0				x	2	1	2
mmm(D_{2h})*							x	x		x	7	3	2
$mm2$(C_{2v})*							0	x		x	3	2	3
222 (D_2)*									x	x	2	2	2
$2/m$ (C_{2h})*								x	x	x	4	3	1
m (C_s)*								0		x	1	1	1
2 (C_2)*									0	x	1	1	1
$\bar{1}$ (C_i)*										x	1	1	0
1 (C_1)*										0	0	0	0

x Subgroup other than original point group.
0 Original point group is a permissible subgroup of itself under vector field.
x—Indicates nonnormal subgroup.
* Cyclic parent, all subgroups normal.

Table 2.3 also shows that some groups can occur as their own subgroups under the action of electric field while others cannot. This distinguishes between cases in which it is possible to apply a suitably oriented electric field which will excite no relaxation mode (except, of course, the trivial mode) and other cases in which any field no matter what its orientation will excite a nontrivial mode. It should be noted that if a purely arbitrary direction of the stress axis be chosen, it can always be arranged that no symmetry elements exist in common with the unstressed point group and the stress, so that the symmetry is reduced to the identity operation 1, and all modes are excited. The application of a homogeneous tensor stress to a centrosymmetric crystal can reach $\bar{1}$, so that any centrosymmetric mode can be excited. These results have their parallel in the expansion of the thermodynamic potential of a crystal in terms of elastic, dielectric, piezoelectric, electrostrictive, etc., coefficients, including higher order terms.

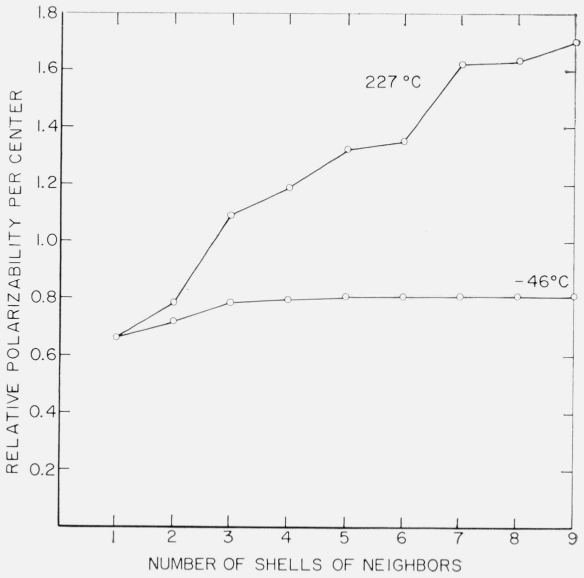
The ability of a suitably oriented electric field to excite all relaxation modes does not conflict with the classification of modes by Haven and van Santen [1, 2] into electrically active, mechanically active, etc., provided that their classification is taken to mean the modes which are most strongly excited by the appropriate influence with the understanding that other modes may be less strongly excited. One can understand how this occurs by considering the effect of an electric field upon an electrically active mode and upon a mechanically active mode. The effect of a static electric field is to shift the energy levels of the sites. These energy shifts, E_j, affect the occupation probabilities exponentially through their appearance in Boltzmann factors; each exponential can be expanded in a power series and only the first few terms kept if the energy shift is small compared to kT. The zeroth order terms are each multiplied by the shift in occupation probability for the corresponding site and then summed to give the change in potential energy. For an electrically active mode (one with a dipole moment) the sum will not be zero, and the mode will be excited to first order in the field; for a mechanically active mode, the sum must be exactly zero because the mode is centrosymmetric so that the mode will not be excited to first order in the field. However, the second order terms from the power series will all be of the same sign and when multiplied by a centrosymmetric pattern of occupation probability and summed, these will give a nonzero result so that a mechanical mode can be excited in second order by an electric field. This line of argument leads to the following rule for the excitation of relaxation modes in terms of their lowest order nonzero moments: Modes having a dipole moment can be excited in the first order by electric field; those with a quadrupole moment can be excited in the first order by mechanical stress or in the second order by electric field; those having an octapole moment can be excited in the third order by electric field; those having a 16-pole moment can be excited in the second order by mechanical stress and in the fourth order by electric field.

Chang [22] has recently tabulated the mechanical modes (in the above sense) for paired point defects in a number of structures with m3m point group symmetry.

3. Dielectric Relaxation in NaCl Containing Divalent Impurity Ions

In order to assess as realistically as possible the influence of the third shell on the dielectric behavior of a real system, we have calculated the dielectric relaxation times and polarizabilities using jump frequencies estimated to correspond to a vacancy trapped near a Mn^{++} ion in NaCl, and employing the results of the present paper. The jump frequencies were chosen as follows. It was assumed that the jump frequency from the ith to the jth site could be given by $w_{11} \exp [(E_j - E_i)/2kT]$, where the E_j are the binding energies of the various sites, and the w_{11} is the jump frequency in the first shell. Furthermore, following Haven [21], w_{33} was taken to be $\frac{1}{3}\, w_{11}$ and w_i was neglected. For the binding energies, the value of 0.41 eV given by Watkins [23] for the first shell was used, and the value of 0.38, derived from his determination of 0.034 eV as the difference in binding energies between the first and second shells, was chosen for the latter. Coulombic energies were plotted for the first nine shells, and a

FIGURE 1. *Relative polarizabilities for the matched point defect pair, in units of $(ea)^2/kT$ where e is the charge on each defect and a is the nearest neighbor distance, for models allowing from 1 to 9 shells of neighbors.*



smooth curve drawn through Watkins two values and joining the Coulombic curve at and above the fifth shell. Temperatures of −46° and 227° C were chosen to match the experimental ranges of Dreyfus [12] and Watkins [23] respectively.

With these values for the binding energies, an estimation of the polarizability per center could be made for models allowing access to various numbers of shells of neighbors. The relative polarizabilities per center, in units of $(ea)^2/kT$ where e is the charge per defect and a is the distance between nearest neighors, are shown in figure 1 for the two temperatures. At −46 °C, little error is made in stopping at the third shell, but at 227 °C, the magnitude of the polarizability is at least three times that estimated from a single shell of neighbors. The influence of outer shells certainly cannot be neglected, at least at the higher temperatures.

The contribution of each of the electrically active modes to the total polarizability is given in table 3.1. The outstanding feature is the dominance of the slowest mode. This contributes 96 percent of the total polarizability at both −46 °C and 227 °C, and leads to the conclusion that a Debye peak would result from an a-c study of the dielectric relaxation with an apparent single relaxation time, even if the influence of the third shell were included.

In the present calculation, the third shell contributed 46 percent of the polarizability at 227 °C, and 10 percent at −46 °C. It appears that the dominance of one mode in the polarizability may be a general feature of these models, regardless of the number of shells included.

The effect of temperature upon the relaxation can be seen from the figures in table 3.1.

TABLE 3.1. *Dielectric relaxation of 3-shell model*

	Relaxation rate		Contribution to polarizability	
Mode	−46 °C	227 °C	−46 °C	227 °C
1	2.38 w_{11}	2.07 w_{11}	96.0%	96.5%
2	11.14 w_{11}	6.31 w_{11}	2.7	0.5
3	14.21 w_{11}	8.10 w_{11}	1.2	1.2
4	15.54 w_{11}	10.05 w_{11}	0.1	2.8

4. Summary

The results of a relaxation mode analysis are presented for two cases of trapped-defect relaxation in the NaCl structure, in which both defects occupy the same type of site (e.g., impurity divalent ion and trapped vacancy), or in which they occupy the two different types of sites (vacancy pair). The relaxation analysis is presented in the form of a set of basis vectors in occupation-probability space and a set of secular equations. Solutions to the equations provide the relaxation rates and also the coefficients in the linear combinations of the basis vectors which constitute the relaxation modes.

The modes excited by the application of a given stress can be deduced from the subgroup of the full symmetry group of the crystal reached by action of the stress. Under this subgroup, some of the group representations that were irreducible under the full group become reducible. Some of them contain the A_{1g} irreducible representation of the subgroup as a component. The corresponding modes are then the ones that are excited by the stress.

Calculations of the relaxation rates and contributions to the polarizability of the various modes for a three-shell model with jump frequencies chosen to represent the relaxation of an impurity-ion vacancy pair in NaCl (Mn) have confirmed the results of Lozovskii [13]. Even though the third shell makes a significant and even large contribution to the process, one mode dominates and the relaxation as seen in a-c measurements would take place with essentially a single relaxation time. The d-c techniques of Dreyfus [12] are sensitive enough to detect more than one of these relaxations at low temperatures, but the slowest of these will always be the dominant one. Any relaxation slower than the major one must be ascribed to some other mechanism.

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