Density of States Information from Low Temperature Specific Heat Measurements*

Paul A. Beck and Helmut Claus

University of Illinois, Urbana

The calculation of one-electron density of state values from the coefficient γ of the term of the low temperature specific heat linear in temperature is complicated by many-body effects. In particular, the electron-phonon interaction may enhance the measured γ as much as twofold. The enhancement factor can be evaluated in the case of superconducting metals and alloys. In the presence of magnetic moments, additional complications arise. A magnetic contribution to the measured γ was identified in the case of dilute alloys and also of concentrated alloys where parasitic antiferromagnetism is superimposed on an over-all ferromagnetic order. No method has as yet been devised to evaluate this magnetic part of γ. The separation of the temperature-linear term of the specific heat may itself be complicated by the appearance of a specific heat anomaly due to magnetic clusters in superparamagnetic or weakly ferromagnetic alloys.

Key words: Alloys; density of states; low temperature specific heat; magnetic specific heat; many-body effects; superconductivity.

1. Introduction

In the Sommerfeld-Bethe theory of metals the electronic specific heat at low temperatures is linear in temperature in first order approximation. The lattice specific heat in the low temperature approximation is proportional to T^3 so that, in the absence of other contributions, the total specific heat

$$C = \gamma T + \beta T^3 \qquad (1)$$

If C is known as a function of T, the two terms can be separated by making use of the linear variation of C/T with T^2 and by extrapolating to $T = 0$. The intercept of the extrapolated line with the ordinate axis gives the temperature coefficient of the electronic specific heat γ. In the simplest case, γ is proportional to the electronic density of states at the Fermi surface, $N(E_F)$:

$$\gamma = (1/3)\pi^2\alpha k^2 N(E_F) \qquad (2)$$

where k is the Boltzman constant and α is a numerical

factor determined by the units used for γ, $N(E_F)$ and k.

Unfortunately, in a very large majority of cases, the simple procedure just described cannot be used, or at least it does not give reliable results. Many-body effects and, in some alloys, magnetic effects may make the determination of $N(E_F)$ from low temperature specific heat data more complicated than implied by eqs (1) and (2), or even impossible at the present state of the art.

2. Many-body Effects

In recent years it has become known that many-body effects, in particular the electron-phonon interaction, require renormalization of the effective mass of the electrons at the Fermi surface. This increases the measured electronic specific heat coefficient over the one-electron "band structure" value by the enhancement factor $(1 + \lambda)$. For Na, Al and Pb, it was possible to determine the value of this factor [1], by comparing the "band structure electronic specific heat," calculated from the known band structure and the topography of the Fermi surface, with the measured electronic specific heat. These values: 1.25, 1.45 and 2.00, respectively, were found to agree quite well with the enhance-

ment factors calculated from band structure, Fermi surface topography and phonon dispersion curves, on the basis of the electron-phonon interaction [1]. Unfortunately, for most other metals calculations of this sort cannot be made at present since at least some of the required data are not yet available. For superconducting metals the electron-phonon coupling constant λ has been recently calculated by McMillan [2], using the following equation which he derived from the strong coupling theory:

$$T_C = \frac{\theta}{1.45} \exp - \left[\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right], \qquad (3)$$

where T_C is the superconducting transition temperature and θ is the Debye temperature. The electron-electron interaction constant μ^* was assumed to have a value of 0.13 for all transition metals. The values of λ calculated by McMillan [2] for superconducting metals are given in table I.

TABLE I. *The Electron-Phonon Interaction Coefficient λ and "Band Structure" Density of States* $N(E_F)$ *for Superconducting Metals.*[2]

Element	T_c °K	Θ °K	λ	$N(E_F)$ eV^{-1}atom^{-1}
Be......................	.026	1390	.23	.032
Al......................	1.16	428	.38	.208
Zn......................	.85	309	.38	.098
Ga......................	1.08	325	.40	.091
Cd......................	.52	209	.38	.106
In......................	3.40	112	.69	.212
Sn......................	3.72	200	.60	.238
Hg......................	4.16	72	1.00	.146
Tl......................	2.38	79	.71	.182
Pb......................	7.19	105	1.12	.276
Ti......................	.39	425	.38	.51
V......................	5.30	399	.60	1.31
Zr......................	.55	290	.41	.42
Nb......................	9.22	277	.82	.91
Mo......................	.92	460	.41	.28
Ru......................	.49	550	.38	.46
Hf......................	.09	252	.34	.34
Ta......................	4.48	258	.65	.77
W......................	.012	390.	.28	.15
Re......................	1.69	415	.46	.33
Os......................	.65	500	.39	.35
Ir......................	.14	420	.34	.51

It is now clear that the enhancement factor $(1 + \lambda)$ of the electronic specific heat due to the electron-phonon interaction can be as high as 2, or more. This interaction affects only the electrons whose kinetic energy is close to the Fermi energy. The density of states at lower levels, that is for most of the electrons in the metallic band, may be assumed to correspond to the one-elec-

tron "band structure" situation. Hence, the lower, "band structure density of states" values must be used in determining the band width, for instance, rather than the density of states enhanced by electron-phonon interaction, as obtained from low temperature specific heat measurements. Using the electron-phonon coupling constant λ, for instance the values given in table I, the "band structure density of states" at the Fermi level $N(E_F)$ can be calculated from the experimentally determined value of the low temperature specific heat coefficient γ' as follows:

$$N(E_F) = \frac{3}{\pi^2 k^2 \alpha (1+\lambda)} \gamma' \qquad (4)$$

For most of the nonsuperconducting metals and alloys the value of λ is at present unknown and, as a result, the "band structure density of states" cannot be calculated from the low temperature specific heat.

As seen in figure 1, the experimental electronic specific heat coefficient γ' for the b.c.c. 3d-transition metals and their alloys as a function of electron concentration [3] shows prominent maxima and minima in the range of e/a from 4 to 9. Since in the region of the minima and of the second maximum the alloys are not superconducting, the "band structure density of states" cannot be calculated at present. Thus, the interesting question whether the prominent features of these curves are due to changes in the electron-phonon enhancement factor upon alloying, or indeed these features are characteristic of the electronic band structure of the transition metals concerned, cannot be answered
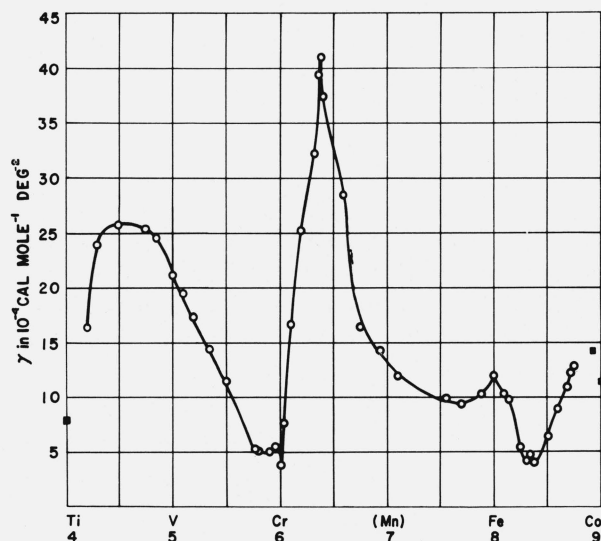

FIGURE 1. *Coefficient γ' or γ'' of the low temperature specific heat term linear in temperature vs electron concentration e/a for b.c.c. alloys of 3d transition metals [3]. Points marked by filled squares represent data for close-packed structures.*

450

with certainty. However, the work of McMillan [2] allows the conclusion that the electron-phonon coupling constant (and, thus, the enhancement factor) depends primarily on the phonon frequencies, rather than on the electronic properties. Since the elastic constants and, therefore, the phonon frequencies are not known to undergo drastic changes with the composition in such solid solution alloys composed of metals near one another in the same row of the periodic table, it may be concluded with a reasonable degree of probability that the prominent features mentioned of the γ' versus e/a curve of figure 1 are in fact resulting from corresponding variations in the "band structure density of states," even though the relative magnitude of the various minima and maxima may be appreciably altered by the gradual changes in the coupling constant with composition.

3. Magnetic Effects

Considerable difficulties are often encountered in determining the value of γ' for solid solution alloys of ferromagnetic with antiferromagnetic or nonmagnetic metals. For instance, it was found [4] for the random solid solution alloys Mn-Ni that, in addition to the electronic specific heat coefficient γ', the measured coefficient γ'' of the term of the low temperature specific heat linear in temperature includes also a magnetic contribution γ_m:

$$\gamma'' = \gamma' + \gamma_m. \qquad (5)$$

The alloy $MnNi_3$ can be ordered by thermal treatment and, in the well-ordered condition, the coefficient of the linear term of the low temperature specific heat is approximately half that for the disordered alloy of the same composition. This lower value is substantially free of the magnetic contribution γ_m and it may be considered as approximately equal to the real experimental electronic specific heat γ' of the alloy. On the other hand, the larger γ'' value for the disordered alloy includes γ_m. Similar magnetic contributions to γ'' were identified in a number of other f.c.c. solid solution alloy systems [4] and in b.c.c. Fe-Al alloys [5]. It is significant that in the same alloy systems, and at similar compositions, magnetic measurements by Kouvel [6,7] detected the appearance of an asymmetrical hysteresis loop after cooling in a magnetic field through the Curie temperature ("exchange anisotropy"). In addition to this effect of field cooling on the magnetic properties, in several instances an effect of field cooling on γ_m was also detected [4,8], figure 2.
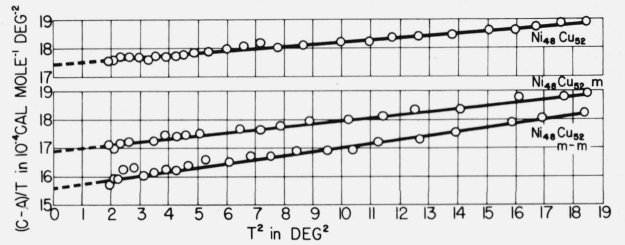

FIGURE 2. $(C-A)/T$ vs T^2 *(where C-A is low temperature specific heat less magnetic cluster contribution, see eq (5)) for alloy $Ni_{0.48}Cu_{0.52}$ cooled without a magnetic field (top graph), cooled in 14 kOe field from 300 to 4.2 K with the field turned off during the measurements (graph* m) *and field-cooled with the field on during measurements (graph* m − m) [8].*

The occurrence in the same alloys of "exchange anisotropy" and of a magnetic contribution to the low temperature specific heat term linear in temperature suggests that these two phenomena may be associated with the same structural condition. This expectation is further supported by the fact that γ_m is normally also affected by field cooling. According to Kouvel's highly successful model [7], the structural condition responsible for "exchange anisotropy" is a spatially inhomogeneous magnetic state, e.g., the superposition of local "parasitic antiferromagnetism" on net overall ferromagnetism. Overhauser [9] and Marshall [10] connected the magnetic contribution to the linear term of the low temperature specific heat with the location of a sufficient number of spins in a near-zero field. In Overhauser's theory this condition arises at the nodes of the static spin density waves of an antiferromagnet. Marshall pointed out that the required condition may arise in dilute spin systems, where the average distance between neighboring spins is sufficiently large, so as to make the interactions weak, as in dilute Cu-Mn alloys. The alloys considered above are neither antiferromagnetic nor dilute. However, because of the peculiar, complicated spin arrangement, resulting from the superposition of local parasitic antiferromagnetism on net overall ferromagnetism, it may be expected that many spins are located in small regions where ferromagnetic and antiferromagnetic exchange interactions nearly cancel each other locally, so that the average field in such regions is near zero [4]. In accordance with this "local field-cancellation" model, the effect of field cooling on γ_m may come about if the application of an external magnetic field during cooling through the Curie temperature increases or decreases the number of spins located in near-zero field. Both increase and decrease [($MnNi_3$ [4], $Ni_{0.48}Cu_{0.52}$ [8])] were in fact observed. It is easy to visualize that the change in γ_m as a result of field cooling may also happen to be negligibly

small, even though the value of the magnetic contribution γ_m itself is large. Thus, while the occurrence of a measurable effect of field cooling on the temperature-linear term of the low temperature specific heat may be considered as a proof for the existence of a magnetic contribution to this term, the absence of such an effect does *not* prove that γ_m is zero, or that it arises through a mechanism different from the "local field cancellation."

If the experimentally determined coefficient of the temperature-linear term of the low temperature specific heat includes a magnetic contribution, it is at present not possible to derive from such a γ'' value the "experimental electronic specific heat coefficient" γ', which is free from γ_m. This is well illustrated by the Ni-Cu alloys, for which the coefficient of the linear term has a maximum around the composition $Ni_{0.48}Cu_{0.52}$ [8]. A detailed study of the properties of these f.c.c. solid solutions at compositions in the vicinity of the maximum [11] shows that the experimental values of the coefficient do in fact include a magnetic contribution. It is, therefore, not possible to tell whether the maximum is entirely due to γ_m, or whether γ' itself has a maximum, which is merely increased by the addition of γ_m. A maximum in γ' has been expected on theoretical grounds [12] because of enhancement due to the electron-paramagnon interaction [13,14]. The theory
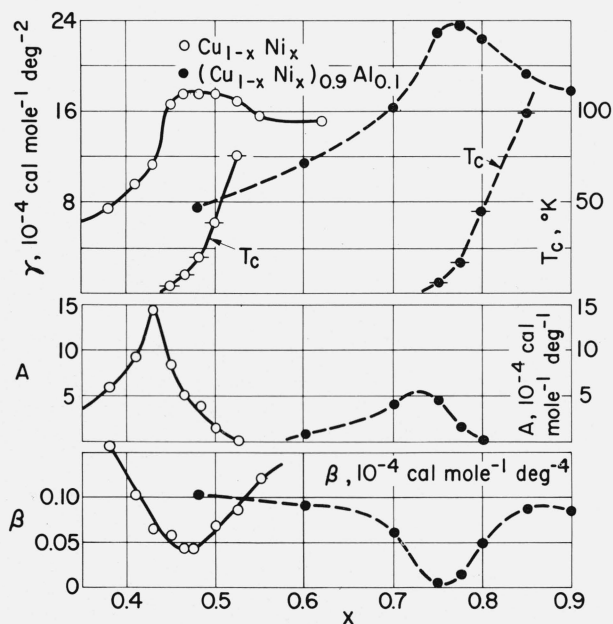
FIGURE 3. *Coefficient γ'' of the temperature-linear low temperature specific heat term, Curie temperature T_C, temperature independent specific heat term A and coefficient β of the T^3 term, obtained by least squares fitting to eq (5), for $Cu_{1-x}Ni_x$ (solid lines) and for $(Cu_{1-x}Ni_x)_{0.9}Al_{0.1}$ (dashed lines) alloys vs x [11,22,24].*
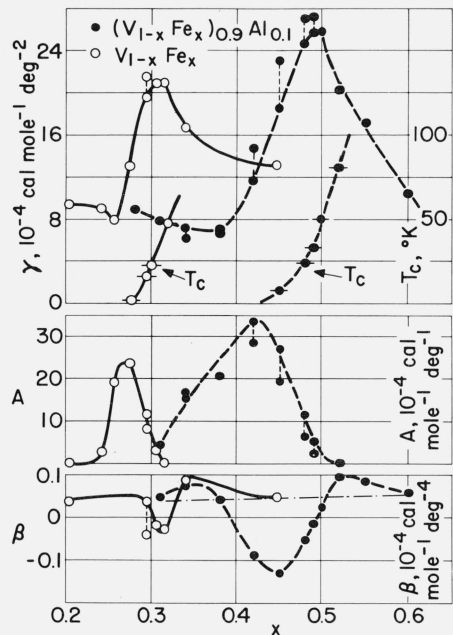
FIGURE 4. *Low temperature specific heat and Curie temperature data, as in figure 3, for $V_{1-x}Fe_x$ (solid lines) and $(V_{1-x}Fe_x)_{0.9}Al_{0.1}$ (dashed lines), alloys [3,23,24].*

would require the maximum of γ' to occur at the critical composition, where ferromagnetism just begins to set in at 0 K. Detailed study of the magnetic properties showed [11] that the critical composition is at approximately 57 percent Cu, where γ'' already decreased to a value far below its maximum. Figure 3 gives γ'' for the Ni-Cu solid solutions, together with Curie temperature data, which define the critical composition. One may conclude that the maximum in γ'' is largely, or entirely, due to γ_m, rather than to γ'. That the maximum in γ_m should occur in the weakly ferromagnetic region is entirely consistent with the "local field cancellation" model discussed above. It is quite likely that the maximum in the coefficient of the linear term for the f.c.c. Rh-Ni solid solutions, which apparently also occurs off the critical composition on the ferromagnetic side [15,16], is also due to a magnetic contribution γ_m. In fact, several solid solution alloy systems are now known to exhibit similar conditions. Figure 3 shows this for a series of Ni-Cu-Al ternary alloys with a constant Al-content of 10 percent. It is seen that the Al addition shifts the critical composition to a higher Ni/Cu ratio, that the maximum in γ'' (which is here even higher than for the binary alloys) is also shifted, and that it again appears away from the critical composition, on the ferromagnetic side. Further examples are given in figure 4, which shows similar data for b.c.c. V-Fe binary and V-Fe-Al ternary solid solutions with a constant Al-content of 10 percent.

452

As yet there appears to be no experimental evidence for the theoretically predicted [14] peak in γ' in alloys at the critical composition, resulting from the electron-paramagnon interaction.

Figures 3 and 4 illustrate also a complication, which arises quite frequently in extracting the coefficient of the temperature-linear term from low temperature specific heat data for weakly ferromagnetic and almost ferromagnetic alloys. In many alloy systems in a certain region around the critical composition an anomaly in the measured low temperature specific heat is observed, so that C is no longer given by eq (1). This anomaly is conspicuously evident in the usual C/T versus T^2 graph. Instead of being a straight line, this graph becomes a curve, extending upward at low temperatures. It was shown by Schroeder [16] that, in such cases, eq (1) can be usually replaced by

$$C = A + \gamma T + \beta T^3. \qquad (6)$$

Schroeder found that the addition of a temperature-independent term A to the low temperature specific heat results from the thermal excitation of magnetic clusters present in many nearly ferromagnetic and weakly ferromagnetic alloys. The presence of magnetic clusters in Ni-Cu alloys in the composition range 50-56 percent Cu has been recently beautifully documented by Hicks, Rainford, Kouvel, Low and Comley [17] by means of neutron magnetic diffuse scattering. In Schroeder's theory the magnetic clusters, which interact with a weak crystal field, are thermally excited and they contribute an Einstein specific heat, which is temperature-independent above the Einstein temperature. The temperature range of 1.4 to 4.2 K, frequently used in low temperature specific heat measurements, appears to be above the Einstein temperature in most such systems. Investigations by Scurlock [18] show a decrease at lower temperatures of the anomalous specific heat from its constant value above 1.4 K, suggesting that the Einstein temperature is near 1.4 K. Since A includes an equal contribution of k for each cluster, regardless of the cluster moment [16], the low temperature specific heat data, from which the value of A can be extracted by least squares fitting to eq (6), give reliable information as to the number of thermally excited magnetic clusters. The correlation of the number of clusters for Ni-Cu alloys by specific heat measurements [11] with the number of clusters derived from neutron scattering [17] is given in figure 5. It is seen that the low temperature specific heat data for the superparamagnetic alloys (Cu-content larger than 57%) are quite consistent with the neutron scattering data. For the weakly ferromag-
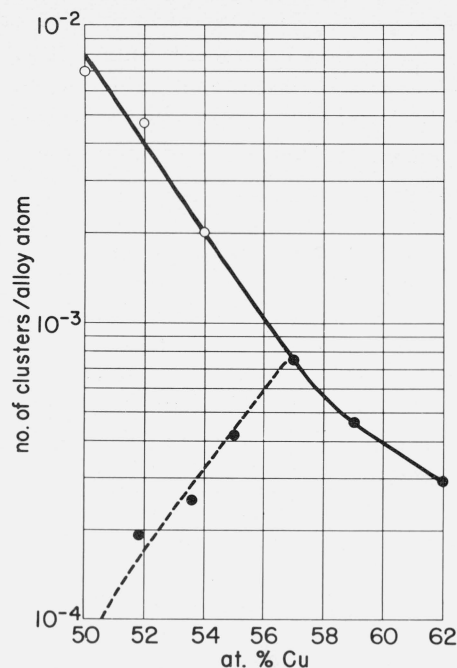

FIGURE 5. *Concentration of magnetic clusters in Ni-Cu alloys vs composition* [22]. *Filled circles represent cluster concentrations calculated from specific heat data. Empty circles give magnetic cluster concentrations derived from neutron magnetic diffuse scattering* [17].

netic alloys the number of thermally excitable clusters rapidly decreases with increasing Curie temperature (decreasing Cu-content). In this composition range most of the magnetic clusters interact with one another and become part of the ferromagnetic system. As seen in figures 3 and 4 the maximum of A corresponds well with the critical composition for all four alloy systems considered. Figures 3 and 4 also show the anomalous behavior of the parameter β, obtained by least squares fitting to eq (6). The anomalous variation of β with composition occurs in all four alloy systems in the vicinity of the critical composition, and it is clearly magnetic in origin [5].

4. Nuclear Specific Heat Effects

It was shown by Marshall [19] that the hyperfine interaction between the dipole moments associated with certain nuclides and the effective field H_{eff} at these nuclei, resulting from electronic spin moments, gives rise to a contribution to the low temperature specific heat. This contribution decreases rapidly with increasing temperature; in the 1.4 to 4.2 K range it is proportional to T^{-2} ("high temperature" approximation). Consequently, the nuclear magnetic specific heat term can

be separated easily from the electronic specific heat term γT in that temperature range. The nuclear quadrupole specific heat recently reported by Phillips [20] and by Martin [21] is also proportional to T^{-2} and, thus, poses no problem in determining the electronic specific heat.

5. Acknowledgments

6. References

[1] Ashcroft, N. W., and Wilkins, J. W., Phys. Letters **14**, 285 (1965).

[2] McMillan, W. L., Phys. Rev. **167**, 331 (1968).

[3] Cheng, C. H., Wei, C. T., and Beck, P. A., Phys. Rev. **120**, 426 (1960); and Cheng, C. H., Gupta, K. P., Van Reuth, E. C., and Beck, P. A., Phys. Rev. **126**, 2030 (1962).

[4] Gupta, K. P., Cheng, C. H., and Beck, P. A., J. Phys. Chem. Solids **25**, 73 (1964).

[5] Cheng, C. H., Gupta, K. P., Wei, C. T., and Beck, P. A., J. Phys. Chem. Solids **25**, 759 (1964).

[6] Kouvel, J. S., and Graham, C. D., J. Phys. Chem. Solids **11**, 220 (1959).

[7] Kouvel, J. S., J. Appl. Phys. **30**, 313S (1959) and **31**, 142S (1960).

[8] Gupta, K. P., Cheng, C. H., and Beck, P. A., Phys. Rev. **133**, A203 (1964).

[9] Overhauser, A. W., J. Phys. Chem. Solids **13**, 71 (1960).

[10] Marshall, W., Phys. Rev. **118**, 1519 (1960).

[11] Robbins, C. G., Claus, H., and Beck, P. A., J. Appl. Phys. **40**, 2269 (1969).

[12] Bennemann, K. H., Phys. Rev. **167**, 564 (1968).

[13] Berk, N. F., and Schrieffer, J. R., Phys. Rev. Letters **17**, 433 (1966).

[14] Doniach, S., and Engelsberg, S., Phys. Rev. Letters **17**, 750 (1966).

[15] This is suggested by the data in the following papers, although their authors did not reach this conclusion: Bucher, E., Brinkman, W. F., Maita, J. P., and Williams, H. J., Phys. Rev. Letters **18**, 1125 (1967); and Brinkman, W. F., Bucher, E., Williams, H. J., and Maita, J. P., J. Appl. Phys. **39**, 547 (1968).

[16] Schroder, K., J. Appl. Phys. **32**, 880 (1961).

[17] Hicks, T. J., Rainford, B., Kouvel, J. S., Low, G. G., and Comly, J. B., J. Appl. Phys. **40**, 1107 (1969).

[18] Scurlock, R. G., and Wray, E. M., Phys. Letters **6**, 28 (1963); and Proctor, W., and Scurlock, R. G., Proc. 11th Conf. Low Temp. Phys. (St. Andrews, 1969), p. 1320.

[19] Marshall, W., Phys. Rev. **110**, 1280 (1958).

[20] Phillips, N. E., Phys. Rev. **118**, 644 (1960).

[21] Martin, D. L., Phys. Rev. Letters **18**, 839 (1967).

[22] Robbins, C. G., University of Illinois Thesis, (1969).

[23] Pessall, N., Gupta, K. P., Cheng, C. H., and Beck, P. A., J. Phys. Chem. Solids **25**, 993 (1964).

[24] New measurements by H. Claus, to be reported in detail elsewhere.

(Paper 74A3−611)