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Lattice-Vibrational Properties of Chromium in the Harmonic Approximation on the Basis of the Tensor Model*

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A tensor force model, including up to four nearest-neighbor interactions, which is in satisfactory agreement with inelastic-neutron-diffraction data and with elastic constants, has been obtained. The results of calculations based on this model, of the frequency spectrum and its moments, the specific heat, and the Debye-Waller factor are presented. The concept of equivalent Debye temperatures is used extensively. Results for the thermal properties are believed to be reliable, and are compared with x-ray intensity measurements and with C_p and related thermodynamic measurements. An estimate of the electronic specific heat proposed by Heiniger is employed. Reasonable agreement between theory and experiment is obtained.

INTRODUCTION

NEUTRON measurements of the lattice vibrational dispersion curves in chromium were performed several years ago.[1] But, perhaps because of the relative sparseness of the data, no published Born–von Kármán analysis of the data has appeared in the literature. After we began this work, we noticed a paper by Gilat[2] in which he refers to an unpublished seventh-nearest-neighbor model which he has determined from a precise fit to the neutron data. It was suggested by Möller and Mackintosh[1] that a third-nearest-neighbor model would represent their data well. In this paper we present results based on a fourth-nearest-neighbor tensor force model[3] fit to the neutron data and elastic constants[4,5] at $T=300$°K. In this model the Born–von Kármán theory is assumed to apply, the lattice structure is taken into account, and all interactions beyond fourth-nearest-neighbor atoms are assumed to be zero. Although the model may represent a substantial simplification of the lattice dynamics of chromium, we believe that the thermal properties, which do not depend on the detailed shape of the frequency spectrum, can be determined to a reasonable accuracy from it. Thus we present calculations of the frequency spectrum, of its moments, of the heat capacity, and of the Debye-Waller factor, with extensive use of the concept of equivalent Debye temperatures. We compare our calculations with the most recent experimental x-ray and thermodynamic data. Furthermore, our work may be generally useful in studies involving the lattice dynamics of chromium.

In order to compare our heat capacity results with experiment for most temperatures of interest, it is necessary to consider the following: the C_p-C_v correction; other anharmonic effects; the electronic specific heat; and the spin-wave contribution to the specific heat, where it is assumed that these effects contribute additively to the specific heat. Except for our knowledge of quasiharmonic effects, which seem to be relatively small for chromium (about a 0.5% effect in Θ between $T=70$ and 370°K), we have no reliable information on anharmonic effects in C_v. However, the small C_p-C_v correction, determined from available thermodynamic data, and a crude estimate from high-temperature data, suggest that explicit anharmonic effects in C_v are approximately only 1% of the total heat capacity at the highest temperatures which we consider.

In estimating the electronic contribution to the specific heat, it is important to consider studies which have elucidated both the electronic structure and the origin of the antiferromagnetism of chromium.[6–10] On the basis of these studies, as Heiniger[11] has shown, a reasonable estimate of the electronic specific heat is given by the equations

$$C_e=\gamma_a T+C_{es}(T,T_N,\gamma')\,,\quad T\leq T_N$$

and (1)

$$C_e=\gamma_p T\,,\quad T>T_N$$

where $\gamma'=\gamma_p-\gamma_a$. The term C_{es} is the BCS expression for the specific heat of a superconductor. The quantities T_N and γ' are, respectively, the Néel temperature and essentially the density of single-particle states determined from the "magnetic"[9] portion of the Fermi

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[1] H. B. Möller and A. R. Mackintosh, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1965), Vol. I, p. 95.

[2] G. Gilat, Phys. Rev. **157**, 540 (1967). We mention here that with the aid of a simple analytic model we have demonstrated that certain considerations, such as the geometry of the constant frequency surface, $\omega=\omega_H$, and the exact wave-vector dependence of $|\nabla\omega|$, in addition to those given in this paper are required for a discussion of the possible existence of an infinity in the frequency spectrum, $G(\omega)$. We have benefitted from helpful communications with Dr. Gilat on this point.

[3] G. H. Begbie and M. Born, Proc. Roy. Soc. (London) **A188**, 179 (1947).

[4] D. I. Bolef and J. de Klerk, Phys. Rev. **129**, 1063 (1963).

[5] A. Sumer and J. F. Smith, J. Appl. Phys. **34**, 2691 (1963).

[6] A. W. Overhauser, Phys. Rev. **128**, 1437 (1962).

[7] W. M. Lomer, Proc. Phys. Soc. (London) **80**, 489 (1962).

[8] P. A. Fedders and P. C. Martin, Phys. Rev. **143**, 245 (1966).

[9] D. B. McWhan and T. M. Rice, Phys. Rev. Letters **19**, 846 (1967).

[10] A. S. Barker, B. I. Halperin, and T. M. Rice, Phys. Rev. Letters **20**, 384 (1968).

[11] F. Heiniger, Physik Kondensierten Materie **5**, 285 (1966). I am grateful to Dr. T. M. Rice for suggesting the use of Heiniger's estimate of the electronic specific heat.

surface. In the expression for C_{es}, T_N, and γ' are identified with the critical temperature and the normal state specific-heat coefficient. This type of term arises according to the two-band model[6–10] because of the formation of electron-hole pairs, bound by the exchange interaction, over the "magnetic" portion of the Fermi surface. The quantities γ_a and γ_p can be determined from low-temperature heat-capacity data on pure chromium and paramagnetic chromium alloys, respectively, where the latter data must be extrapolated to the artificial case of pure paramagnetic chromium at low temperatures and atmospheric pressure. Thus Heiniger[11] has found that the electronic specific heat for chromium deviates markedly from the usual linear temperature dependence. It is interesting to note that prior to the theoretical investigations cited here, a deviation of C_e from the usual γT dependence was noted in analyses of C_p data.[12,13] More significantly, Heiniger (as well as Fedders and Martin[8]) has shown that the discontinuity in the electronic specific heat at the Néel temperature is approximately equal to the experimental value of the discontinuity in C_p.[14] A different approach to the determination of C_e for chromium has been taken by Shimizu *et al.*[15] However, we consider only Heiniger's treatment in the remainder of this paper.

Fedders and Martin[8] have shown that the spin-wave spectrum of chromium is expected to resemble that of an antiferromagnetic insulator. The spin-wave spectrum of a chromium-manganese alloy has been studied most recently by Sinha *et al.*,[16] using neutron diffraction techniques at $T=300°\mathrm{K}$. Using their results, which should also be valid for pure chromium,[17] and assuming a linear dispersion law, the spin-wave spectrum can be characterized by a wave velocity of $v=1.29\pm26\times10^7$ cm/sec. It can easily be shown that this value of v corresponds to a Debye temperature of about 16 000°K for chromium, and hence will necessarily lead to a negligible spin-wave contribution to the specific heat.

Gilat and co-workers[18] have developed a method for computing very accurate frequency spectra, given the force model, for several types of lattices; in this paper we apply Gilat and Raubenheimer's[18] method to chromium. To a limited extent we have studied the dependence of our results on the force model by using several fourth-nearest-neighbor force models obtained by varying the relative weights of the experimental points in our least-squares analysis. We have found that the thermal properties and the moments of the frequency spectrum were affected only slightly by any changes in the force constants, but that the shape of the frequency spectrum was greatly affected when certain data in the [111] direction were omitted from the analysis.

THEORY

The lattice contributions to the thermal properties discussed in this paper are given by the following expressions in the harmonic approximation:

$$C_L{}^h=k\sum_{\mathbf{f},j}\frac{x^2e^x}{(e^x-1)^2} \tag{2}$$

and

$$X=\sum_{\mathbf{f},j}\frac{e_{\mathrm{vib}}}{\omega^2(\mathbf{f},j)}\,. \tag{3}$$

Here,

$$x=\hbar\omega(\mathbf{f},j)/kT$$

and

$$e_{\mathrm{vib}}=\tfrac{1}{2}\hbar\omega(\mathbf{f},j)+\hbar\omega(\mathbf{f},j)/(e^x-1)\,.$$

The quantity X is proportional to the exponent of the Debye-Waller factor, $\omega(\mathbf{f},j)$ is the angular frequency corresponding to the normal mode of wave vector **f** and polarization index j, and the sum goes over all the normal modes of the crystal. The expressions for X and C_V in the Debye approximation are obtained by rewriting the right-hand sides of (2) and (3) in terms of integrals over the Debye frequency spectrum. The $\omega^2(\mathbf{f},j)$ $(j=1,\ 3)$ are determined as the eigenvalues of the dynamical matrix:

$$D_{\alpha\beta}=-\frac{2}{M}\sum_{\mathbf{l}}\Phi_{\alpha\beta}(\mathbf{l})\sin^2\tfrac{1}{2}(\mathbf{f}\cdot\mathbf{r}_{\mathbf{l}})\,,\quad \alpha,\beta=1,\ 3 \tag{4}$$

where M is the atomic weight, $\mathbf{r}_{\mathbf{l}}$ is the equilibrium position vector of the atom at the **l**th lattice site, and $\Phi_{\alpha\beta}(\mathbf{l})$ is a force constant.

All calculations were performed on a high-speed computer. The sums in Eqs. (2) and (3) were performed by sampling a cubic grid of 1632 points in 1/48th of the Brillouin zone. Other cubic grids were also considered in order to check the accuracy of our results, and on this basis the Debye temperatures given in this paper are believed to be accurate to within 0.4%.

LATTICE MODEL AND PHONON SPECTRUM

The force constants used in our calculations are shown in Table I. The comparison of the input data with the results based on these force constants is shown in Table II and Fig. 1. The calculated values are slightly outside the error limits for some of the elastic constants, but, for practically all points, they are well within the error limits of the neutron measurements. The deviations between the calculated frequencies and the neu-

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[12] D. Armstrong and H. Grayson-Smith, Can. J. Res. **A28**, 51 (1950). The apparent temperature dependence of the electronic specific-heat coefficient was also noted by E. P. Wohlfarth, Rev. Mod. Phys. **25**, 211 (1953).

[13] V. K. Clusius and P. Franzosini, Z. Naturforsch. **17a**, 522 (1962).

[14] R. H. Beaumont, H. Chihara, and J. A. Morrison, Phil. Mag. **5**, 188 (1960).

[15] M. Shimizu, T. Takahashi, and A. Katsuki, J. Phys. Soc. Japan **17**, 1740 (1962).

[16] S. K. Sinha, S. H. Liu, L. D. Muhlestein, and N. Wakabayashi, Phys. Rev. Letters **23**, 311 (1969).

[17] S. K. Sinha (private communication).

[18] G. Gilat and G. Dolling, Phys. Rev. Letters **8**, 304 (1964); G. Gilat and L. J. Raubenheimer, Phys. Rev. **144**, 390 (1966); G. Gilat and Z. Kam, Phys. Rev. Letters **22**, 715 (1969).

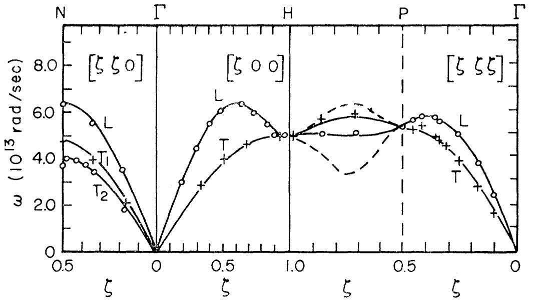

FIG. 1. Dispersion curves. The circles and crosses represent the experimental values (Ref. 1). The solid curves were calculated using force constants obtained by including all neutron and elastic constant data in the least-squares fit. The dashed curves were calculated using force constants obtained when the points in the [111] direction for $\zeta > 0.5$ were omitted from the least-squares fit.

tron measurements vary in magnitude and sign, but for most points the deviations are less than 3% of the frequencies. Also shown in Fig. 1 (dashed curve) are the results obtained when the data in the [111] direction with $\zeta > 0.5$, are omitted from the least-squares analysis. The hope is that by omitting a few well-chosen experimental points in the least-squares analysis, and by carrying out the calculations of the vibrational properties on the basis of the resulting force model, the accuracy of our results can be estimated.

We have also considered an alternate method for analyzing dispersion curves proposed by Rosenstock,[19] first, in order to partially check our assumption that interactions between further than fourth-nearest-neighbor atoms are zero, and second, to help complete the class of systems already studied by this method.[20] In this analysis a body-centered cubic (bcc) monatomic substance is treated as a simple cubic lattice with two atoms per unit cell. The trace of the resulting dynamical matrix can be shown to be dependent only on interactions for which Laplace's equation is not satisfied between second-, third-, fifth-, etc., nearest-neighbor atoms. Thus the data are analyzed by taking sums over the squares of the frequencies for certain pairs of wave-vectors in the Brillouin zone of the bcc lattice (see Refs. 19 and 20 for details), and by comparing the results with those obtained for a particular force model. This comparison has been discussed, and applied to other bcc crystals, on the basis of the axially symmetric model. We point out that for a bcc lattice, the axially symmetric model represents an approximation only for interactions between third-, fourth-, and certain further-than-fifth-nearest-neighbor atoms.

The quantity

$$\Sigma(\mathbf{Q}) = \Big(\sum_{i=1}^{6} \omega^2(\mathbf{Q},i) - \sum_{i=1}^{6} \omega^2(0,i)\Big) \Big/ \sum_{i=1}^{6} \omega^2(0,i)$$

TABLE I. Independent force constants, $\Phi_{\alpha\beta}(\mathbf{l})$, of a fourth-neighbor Born–von Kármán Model (in units of dyn/cm).[a]

		l			
		(1,1,1)	(2,0,0)	(2,2,0)	(3,1,1)
$\alpha\beta$	xx	−16140	−39045	−3350	2045
	yy	xx	1694	xx	381
	zz	xx	yy	401[b]	yy
	xy	−9663	0	−1009	−26[b]
	xz	xy	0	0	xy
	yz	xy	0	0	−587[b]

[a] The entry xy denotes Φxy, etc.

[b] The signs of these force constants are not well determined as other least-square fits gave values deviating from these by more than 100%.

is plotted in Fig. 2 in the [111] direction, where **Q** is a wave vector in the Brillouin zone of a simple cubic lattice. We also obtained $\Sigma(0.6,0,0) = 0.57$, $\Sigma(1,0,0) = 0.91$, and $\Sigma(1,1,0) = 1.27$. Following Rosenstock and Blanken[20] the values of $\Sigma(1,0,0)$, $\Sigma(1,1,0)$ and $\Sigma(1,1,1)$ were used to determine the values $\beta_1 = 0.226$, $\beta_2 = 0.093$, and $\beta_3 = 0.021$, where β_1, β_2, and β_3 are simply related to the forces between second-, third-, and fifth-nearest neighbor atoms, respectively. These values, which are quite similar to those obtained for molybdenum,[20] indicate that fifth-neighbor forces are small. Finally, in order to test the consistency of this analysis, the values of β_i were used to calculate $\Sigma(\mathbf{Q})$, and the results are in satisfactory agreement with experiment (e.g., see Fig. 2).

The frequency spectrum $G(\omega)$ corresponding to the force constants in Table I is given in Fig. 3. The qualitative features of this spectrum are in agreement with those obtained by Leath and Goodman,[21] who used a central-force second-neighbor model in a theoretical study of frequency spectra for disordered alloys.

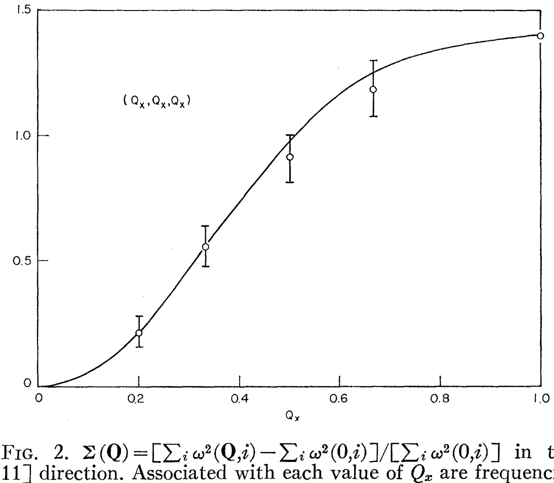

FIG. 2. $\Sigma(\mathbf{Q}) = [\sum_i \omega^2(\mathbf{Q},i) - \sum_i \omega^2(0,i)]/[\sum_i \omega^2(0,i)]$ in the [111] direction. Associated with each value of Q_x are frequencies for wave vectors in the [111] direction with components, $\zeta = \frac{1}{2}Q_x$, $1 - \frac{1}{2}Q_x$ in the Brillouin zone of the bcc lattice. The circles were determined from a tabulation of the neutron data of Ref. 1 and the solid line was calculated using the values $\beta_1 = 0.226$, $\beta_2 = 0.093$, and $\beta_3 = 0.021$. The error bars correspond to our estimated 5% uncertainty in $\omega^2(\mathbf{Q},i)$.

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[19] H. B. Rosenstock, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagen*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965.)

[20] H. B. Rosenstock and G. Blanken, Phys. Rev. **145**, 546 (1966).

[21] P. L. Leath and B. Goodman, Phys. Rev. **181**, 1062 (1969).

TABLE II. Comparison of the force-model results for the elastic constants with the experimental values (ultrasonic) at $T=298°K$ (in units of 10^{12} dyn/cm^2).

	Sumer and Smith[a]	Bolef and de Klerk[b,c]	Fourth-neighbor model
C_{11}	3.398	3.50	3.434
C_{44}	0.990	1.008	1.007
$\frac{1}{2}(C_{11}-C_{12})$	1.406	1.411	1.357
C_{12}	0.586	0.678	0.719

[a] Reference 5.
[b] Reference 5.
[c] Input data to the least-squares fit of the fourth-nearest-neighbor model force constants.

Also shown in Fig. 3 is the frequency spectrum corresponding to the model associated with the dashed curve in Fig. 1. The large difference in shape between the two frequency spectra in the figure leads to, at most, a 2% effect on the Debye temperatures considered in this paper.[22] However, this difference in $G(\omega)$ leads one to suspect the ability of our analysis to provide the correct $G(\omega)$ curve for chromium. As a check on our numerical work, the frequency spectrum of tungsten was calculated for comparison with Gilat's spectrum.[2] The small spike seen at $\omega=3.473\times10^{13}$ rad/sec was also seen in our calculations, but its height was decreased by a factor of 2 and was found to be independent of $\Delta\omega$. This discrepancy may be due to slight differences in programming since only a few normal modes are associated with it.[2]

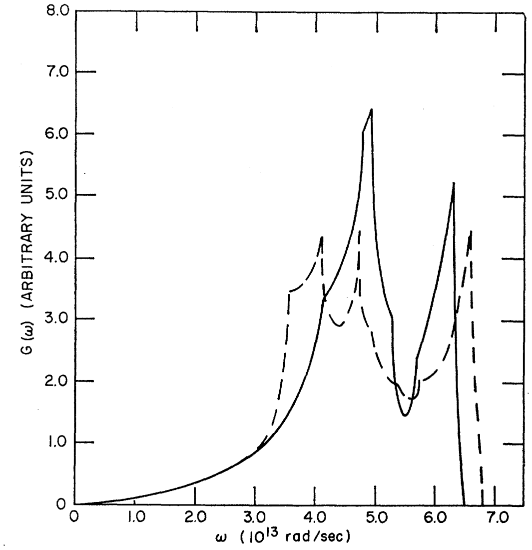

FIG. 3. $G(\omega)$ versus ω. The solid and dashed curves correspond, respectively, to the force constants obtained with the inclusion and exclusion of the data points in the [111] direction for $\zeta>0.5$ in the least-squares fit. The curves represent histograms, with $\Delta\omega=0.0013\times10^{13}$ rad/sec calculated according to Gilat and Raubenheimer's procedure (Ref. 18).

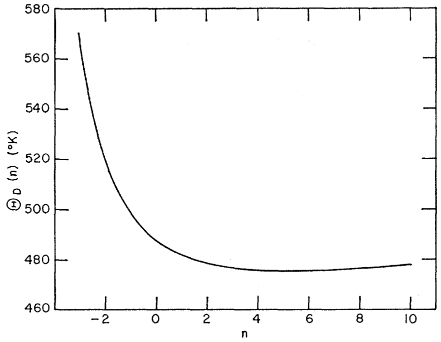

FIG. 4. Barron plot. $\Theta_D(n)$ versus n where $\Theta_D(n)$ is the Debye characteristic temperature associated with the nth moment of the frequency spectrum and with the force constants in Table I. It is noted that for a temperature-independent frequency spectrum, $\Theta_D(n)=\Theta_\infty{}^M$ (for $n=-2$), $\Theta_0{}^M$ (for $n=-1$), $\Theta_\infty{}^C$ (for $n=2$), $\Theta_0{}^C$ (for $n=-3$), etc.

The moments of the frequency spectrum are represented in Fig. 4 by equivalent Debye temperatures in the form of a Barron plot, i.e., $\Theta_D(n)$ versus n, where n refers to the particular moment. For a further discussion of the quantity $\Theta_D(n)$ and of its relevance to the thermal data, the reader is referred to the review article by Salter,[23] and to the caption of Fig. 4. We point out only that for chromium, $\Theta_D(n)$ seems to be fairly constant for $n\geq2$, thus implying constant values of $\Theta^M(T)$, and $\Theta^C(T)$ for $T\geq\Theta_\infty{}^C/2\pi$, which is discussed in the following section.

THERMAL PROPERTIES

In Fig. 5 the Debye temperature which characterizes the Debye-Waller factor is shown. The "experimental" curves were obtained by Wilson, Skelton, and Katz[24] from Bragg x-ray intensity measurements. The three curves correspond to the same data but to three different "reference" Debye temperatures at room temperature. The theoretical curve is similar to those obtained for other materials. As seen in the figure, the theoretical curve is in agreement to within 2% with one of the possible experimental $\Theta^M(T)$ curves over a wide range of temperatures ($100\leq T\leq400°K$). It is not surprising that, above 400°K, the calculation, which is based on the harmonic approximation, is in disagreement with experiment.

The specific heat of chromium is considered in Figs. 6 and 7. It is customary to analyze C_p data at most temperatures with the use of a linear term γT for the electronic specific-heat correction where γ is determined from low-temperature measurements. However, as stated previously, theoretical calculations indicate that this treatment of the electronic specific heat is not valid for chromium. Thus the experimental data were analyzed with the use of Eqs. (1) and a BCS specific-

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[22] We mention here that our value of $\Theta_\infty{}^C$ is in agreement to within 1.6% with the corresponding value which we have obtained using Gilat's unpublished seventh-neighbor model. The quantity $\Theta_\infty{}^C$ represents the high-temperature limit of the specific-heat Debye temperature, Θ^C.

[23] L. S. Salter, Advan. Phys. **14**, 1 (1965).

[24] R. H. Wilson, E. F. Skelton, and J. L. Katz, Acta Cryst. **21**, 635 (1966).

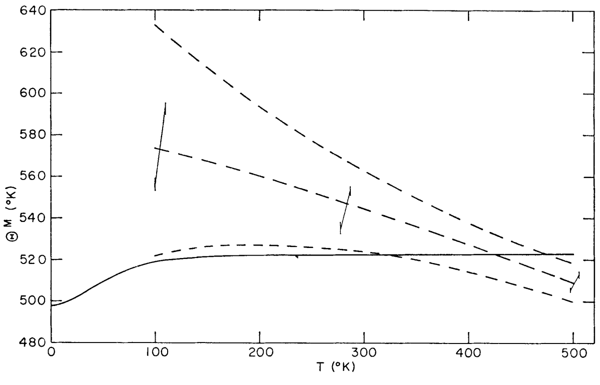

FIG. 5. Θ^M versus T. The solid curve was calculated in the harmonic approximation from our force model. The dashed curves, which were taken from Ref. 24, represent Bragg x-ray intensity measurements by Wilson, Skelton, and Katz. The three experimental curves correspond to the same date with "reference" room-temperature Debye temperatures of 525, 545, and 565°K.

heat table[25] with $\gamma_a=3.6$[13], $\gamma_p=6.9$[11] in cal/mole $°\mathrm{K}^2$ and $T_N=311°\mathrm{K}$. Taking into account discrepancies between values of γ_a, a ±0.2 cal/mole $°\mathrm{K}^2$ uncertainty is associated with the value we use (see Table V of Heiniger *et al.*[26]). However, we have found that this uncertainty does not lead to significant errors in our analysis. Furthermore, it should be noted that γ_a, γ_p, and T_N are volume-dependent[9] and that the values quoted for γ_a and γ_p correspond to the volume at $T=0°\mathrm{K}$, whereas the value quoted for T_N corresponds to the volume at $T=311°\mathrm{K}$. However, we have found that effects of thermal expansion on C_e are at most about 0.1% of the total heat capacity in the temperature range considered in this paper.

The comparison between theory and experiment for the specific heat at temperatures well below the Néel temperature is shown in Fig. 6 by plots of the specific-heat Debye temperature $\Theta^C(T)$. The "experimental" $\Theta^C(T)$ values displayed in the figure correspond to the extracted lattice-vibrational contribution to the heat capacity C_L; we employed the expression $C_V=C_L+C_e$, where we determined C_e from Eqs. (1) and the values of the appropriate parameters quoted earlier, and where we determined C_V from the thermodynamic data of Clusius and Franzosini[13] and Bolef and de Klerk.[4] The reasonable agreement between theory and experiment at $T=0°\mathrm{K}$ is expected, since our model is based in part on the measured elastic constants. Since Θ^C is quite sensitive to the specific heat at moderately high temperatures, the dip in the experimental $\Theta^C(T)$ curve at $T\sim240°\mathrm{K}$ is probably not significant. Also shown in the figure are values of Θ^{el}, determined with the use of de Launay's[27] tables from the elastic constants.[4] The triangle corresponds to the value of Θ^{el} as determined from $T=296°\mathrm{K}$ elastic constants. The difference between this value and our calculated value of $\Theta_0{}^C$, the calorimetric Debye temperature at $T\sim0°\mathrm{K}$, is associated with the least-squares analysis. The square corresponds to the value of Θ^{el} as determined from $T=0°\mathrm{K}$ elastic constants which we obtained by graphical extrapolation from $T=77°\mathrm{K}$. The difference between this latter value of Θ^{el} and Clusius and Franzosini's determination of $\Theta_0{}^C$ is within experimental uncertainty. However, it is worth mentioning that discrepancies exist among different workers as to the value of $\Theta_0{}^C$ at low temperatures (see Table 5 of Heiniger *et al.*[26]).

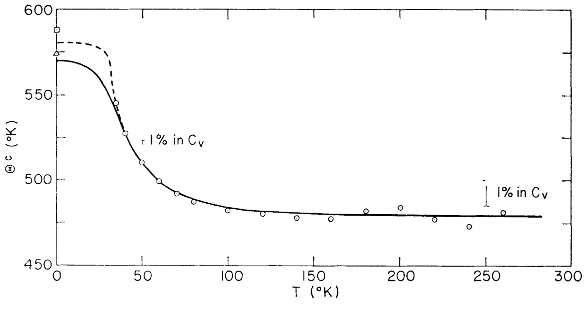

FIG. 6. Θ^C versus T. The solid curve was calculated in the harmonic approximation from our force model. The circles were determined from our analysis (see text) of some of the smoothed experimental C_P data points of Clusius and Franzosini (Ref. 13). The dashed curve was taken directly from Ref. 13. The square and triangle represent the values of Θ^{el} determined, with the use of de Launay's tables, from the $T=0°\mathrm{K}$ (extrapolated from $T=77°\mathrm{K}$) and $T=296°\mathrm{K}$ elastic constants of Bolef and de Klerk (Ref. 4), respectively.

It is also of interest to analyze the specific heat in the region $90°\mathrm{K}\leq T\leq160°\mathrm{K}$ in more detail. In this region, which may be described as $\Theta/2\pi\leq T\leq\frac{1}{3}\Theta$:

(a) The electronic contribution for chromium is estimated to be only about 2% of the total.

(b) The quantity $d\ln\Theta/d\ln C\lesssim1$, so that the Debye temperature is determined at least as accurately as the specific heat.

(c) The Thirring expansion of the harmonic contribution to the specific heat is valid.

(d) Temperature-dependent anharmonic effects in Debye temperatures are expected to be small.[28]

Thus, an accurate value of $\Theta_\infty{}^C$ can be obtained from an analysis of the primary C_p data[13] in this region by considering a $(\Theta^C)^2$-versus-$1/T^2$ plot. We present only the results of this analysis which are $\Theta_\infty{}^C=\Theta_D(2)=478\pm10°\mathrm{K}$, and $\Theta_D(4)=477\pm20°\mathrm{K}$, in excellent agreement with our lattice dynamical calculations of $\Theta_D(2)=478°\mathrm{K}$ and $\Theta_D(4)=476°\mathrm{K}$.

Beaumont, Chihara, and Morrison[14] have performed very precise measurements of C_p between 268 and 324°K. A comparison of our model calculation with the experimental results of Beaumont *et al.*[14] and Clusius

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[25] B. Mühlschlegel, Z. Physik **155**, 313 (1959).

[26] F. Heiniger, E. Bucher, and J. Muller, Physik Kondensierten Materie **5**, 243 (1966).

[27] J. de Launay, J. Chem. Phys. **30**, 91 (1959).

[28] T. H. K. Barron, W. T. Berg, and J. A. Morrison, Proc. Roy. Soc. (London) **242**, 478 (1957). See, also, J. L. Feldman and G. K. Horton, Phys. Rev. **137**, A1106 (1965).

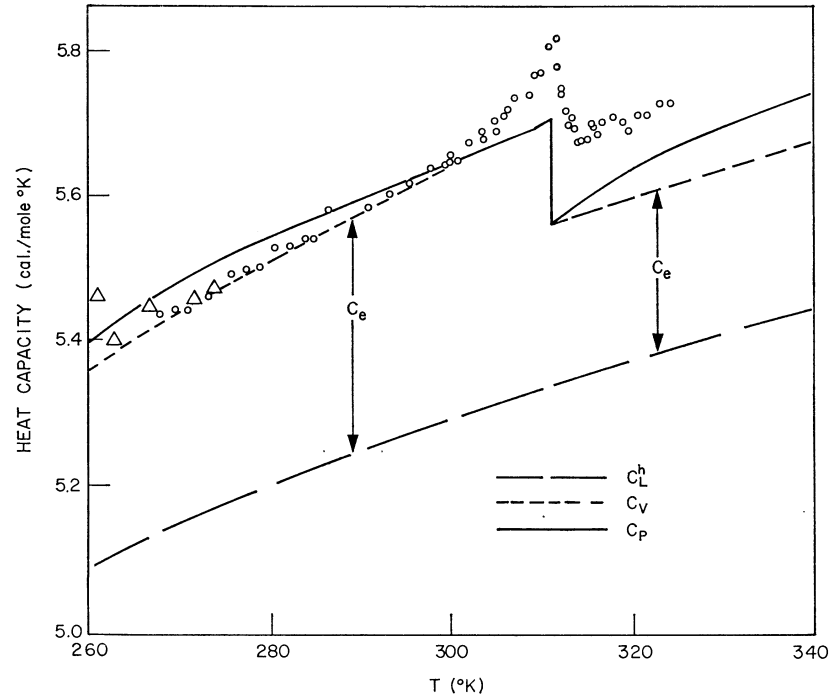

FIG. 7. Contributions to the heat capacity. The quantity C_e was determined from Eqs. (1) of the text. The triangles and circles correspond to primary C_p data taken from Refs. 13 and 14, respectively. A 1% change in Θ^C corresponds to a 0.25% change in $C_L{}^h$ in the temperature region shown.

and Franzosini[13] is shown in Fig. 7. In the antiferromagnetic region of temperatures shown in the figure, C_{es} is approximately 60% of C_e and hence 4% of $C_L{}^h$. A rough estimate of anharmonic effects can be achieved through the use of a one-parameter treatment of anharmonicity.[29] The parameter A that appears in this treatment may be chosen by assuming that the differences between our calculated results for C_v and those derived from high-temperature thermodynamic data[12,30] are anharmonic contributions. Thus we estimate $A \sim -0.5 \times 10^{-4}$°K^{-1}, which corresponds to a 1% anharmonic effect in the temperature region of Fig. 7. Although Figs. 6 and 7 indicate a good over-all agreement between theory and experiment, it is apparent that the models used do not describe the detailed shape of C_p near the Néel temperature. This is not surprising because of the oversimplified nature of the models used.

DISCUSSION

The neutron and ultrasonic measurements of the lattice-vibrational frequencies in chromium have been analyzed in terms of a fourth-neighbor tensor force model in the harmonic approximation. The force constants which this analysis has yielded have been applied to a calculation of the frequency spectrum and its moments, of the specific heat, and of the temperature dependence of the Debye-Waller factor. The agreement with the experimental dispersion curves in most cases is better than 3% in the frequencies. Our results were checked in part by observing the effect of making slight changes in the force constants, by comparing our results with similar studies by Gilat,[2] and by applying Rosenstock's[19,20] method for analyzing neutron data.

The usual Debye temperatures $\Theta^C(T)$ and $\Theta^M(T)$ are plotted, and are found to be very well approximated by constants for $T \geq 100$°K. This behavior in $\Theta^C(T)$ was first suggested by Clusius and Franzosini.[13] The Barron plot, i.e., $\Theta_D(n)$ versus n, which represents the moments of the frequency spectrum, has also been given (Fig. 4). The low- and high-temperature limiting values of $\Theta^C(T)$ and $\Theta^M(T)$ for our model are $\Theta_0{}^C = 569$°K, $\Theta_\infty{}^C = 478$°K, $\Theta_0{}^M = 498$°K, and $\Theta_\infty{}^M = 522$°K.

The results for $\Theta^M(T)$ have been compared with published x-ray experimental values of $\Theta^M(T)$ for $100°\text{K} \leq T \leq 500°\text{K}$ obtained by Wilson, Skelton, and Katz,[24] and it has been seen that our results are not inconsistent with the x-ray values for $T \leq 400$°K. Above this temperature it is likely that the inclusion of anharmonic effects would be necessary to explain the data. The results for the specific heat and $\Theta^C(T)$ have been compared with experiment for $T \leq 325$°K. Near $T = 0$°K our calculation of $\Theta_0{}^C$ necessarily agrees fairly well with experiment since our model is based in part on the measured elastic constants (at $T = 300$°K). We have noted that there exist large uncertainties in the literature as to the value of $\Theta_0{}^C$. We have extrapolated the elastic constants to $T = 0$°K from $T = 77$°K and thus obtained $\Theta_0{}^{el} = 588$°K. This value is in good agreement with the calorimetric result, $\Theta_0{}^C = 580$°K, obtained by Clusius and Franzosini.[13] At moderate temperatures, good over-all agreement with experiment is found with

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[29] J. L. Feldman, G. K. Horton, and J. B. Lurie, J. Phys. Chem. Solids **26**, 1507 (1965).

[30] S. Muller and Ph. Dunner, Z. Naturforsch. **20a**, 1225 (1965).

the use of Heiniger's[11] method for estimating the electronic contribution to the specific heat of chromium. Nevertheless, close to the Néel temperature, there exists a discrepancy (between theory and experiment) as to the shape of the C_p curve which does not appear to be accounted for by reasonable changes in the parameters used in determining C_v. However, in view of the numerous physical assumptions implied by the models used, this discrepancy is not surprising. For example, the electronic model corresponds to a second-order phase transition at T_N, whereas it is known that the transition is first order.[31] Also, effects of a possible temperature dependence of the frequency spectrum due to changes in the electronic structure have been ignored in our lattice model. Such effects in the long-wavelength part of the spectrum seem apparent from the elastic constant data.

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[31] S. A. Werner, A. Arrott, and H. Kendrick, Phys. Rev. **155**, 528 (1967).

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^{115}In NMR in the Indium-Rich Alloys In-Cd, In-Hg, and In-Tl at 4.2°K[*]

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Nuclear magnetic resonance has been observed in the indium-rich alloys In-Cd, In-Hg, and In-Tl at 4.2°K. Measurements have been made of the isotropic Knight shift, anisotropic Knight shift, quadrupole-coupling frequency, and linewidths as a function of solute concentration to 4.7 at.% Cd, 4.3 at.% Hg, and 7.9 at.% Tl. The isotropic Knight shift exhibits a dip similar to that previously observed in In-Sn and In-Pb. The sign of the electric field gradient has been deduced from the quadrupole-coupling frequencies in the alloys, and is negative. The screening theory of Kohn and Vosko is found to describe line broadening in these indium alloys, and the enhancement factor of that theory is determined to be 85 ± 15.

I. INTRODUCTION

IT is possible, in indium metal and its alloys, to obtain the Knight shifts and the electric quadrupolar coupling between indium nuclei and their environment by nuclear-magnetic-resonance measurements. The angular dependence of the anisotropic Knight shift allows its separation from the isotropic Knight shift, while the *m* dependence of the quadrupolar perturbation allows its separation from the *m*-independent Knight shifts. In practice, our measurements are made on metal powders and at a fixed field. Certain difficulties arise in the interpretation of broadened powder-pattern resonance lines. These have been discussed for pure indium by Adams *et al.*[1]

The introduction of substitutional impurities results in long-range screening of the impurities by the conduction electrons.[2–4] This screening produces shifts in the mean or peak absorption frequencies and, in general, asymmetric broadening of the resonance lines. Such broadening and shifts raise questions concerning the measurement and interpretation of resonance lines exhibiting these effects. We shall attempt to clarify the problem by examining the linewidths and line shapes in indium alloys.

In the presence of quadrupole interactions, the addition of a few atomic percent of impurities can easily result in the doubling of the linewidth, providing a good quantitative test of the theories. In this work, we employ the screening theory of Kohn and Vosko,[4] which takes into account the fact that screening electrons are Bloch electrons rather than free electrons, and show how the enhancement factor of the theory can be obtained from the width data. The enhancement factor provides an interesting test of electronic wave functions in a metal, and is necessary for the calculation of line shapes and the contribution of screening to the

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[1] J. E. Adams, B. F. Williams, and R. R. Hewitt, Phys. Rev. **151**, 238 (1966).

[2] J. Friedel, Nuovo Cimento Suppl. **7**, 299 (1958).

[3] A. Blandin and E. Daniel, J. Phys. Chem. Solids **10**, 126 (1959).

[4] W. Kohn and S. H. Vosko, Phys. Rev. **119**, 912 (1960).