

model if Eqs. (17)–(19) correctly describe the electron-lattice interaction.

III. CONCLUSIONS

From Figs. 1–3, one sees that the nature of the electron-lattice interaction becomes increasingly important in determining the frequency dependence with ascending powers of the magnetic field. It appears that any deviation from a constant relaxation time will move frequency-dependent effects to correspondingly lower frequencies. Indeed, with ionized impurity scattering,

the imaginary part of $\beta(\omega)$ reaches its maximum when $\omega(\tau)$ is less than one-tenth.

One would expect intervalley scattering to have a large effect on the frequency dependence for many-valley semiconductors because of the extreme way it influences $\tau(\epsilon)$.⁸ Also, since the theory predicts that the three second-order coefficients have the same frequency dependence when the relaxation time is a scalar function of energy, comparison of these quantities should yield information concerning anisotropy of the relaxation time tensor.

Calculated Vibrational Spectra and Specific Heats of Lithium and Vanadium*

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Vibrational spectra and specific heats have been calculated for lithium and vanadium, from measured elastic constants, on the basis of three different models. Two of the models are of the Born-von Kármán type. One of these considers only central forces between nearest and next-nearest neighbors; the other includes noncentral forces between nearest neighbors and central forces between next-nearest neighbors. The third model is due to de Launay. The calculated quantities from all models are compared with the available empirical values and values calculated by others. It is concluded that none of the models is a satisfactory representation of either metal.

INTRODUCTION

THE availability of measured elastic constants for vanadium and lithium now permits the computation of the vibration spectra of these two metals without having to resort to derived elastic constants. The vibration spectra have been determined using three well-known force models.

In one model the atomic interactions are assumed to be central forces between nearest and next-nearest neighbors in the bcc lattice structure. This model is called the *central model* in this paper. The calculated frequency spectra for 18 values of the ratio of the next-nearest-neighbor force constant to that for nearest neighbors have been reported previously by Clark,¹ and calculations for the specific heats of seven bcc elements were reported later.²

In a second model, interactions of a noncentral nature

between nearest neighbors are considered as well as central interactions between next-nearest neighbors. The model is characterized, then, by 3 force constants. This model has been described by Leibfried,³ for example, and was employed by Singh and Bowers⁴ for the calculation of the spectrum of vanadium; however, their calculations employed elastic constants deduced from low-temperature specific-heat data. This model is referred to as the *noncentral model* in this paper.

The third phenomenological model is due to de Launay.⁵ In this model it is presumed that the conduction electrons in a metal respond in-phase to longitudinal components of lattice waves, but are not influenced by transverse components. This response modifies the force constants so that one set is effective for transverse components and a different set is effective for longitudinal components. This model will be called the *de Launay model* in this paper. (It should be pointed out that de Launay proposed a model which would reduce to this

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¹ C. B. Clark, J. Grad. Res. Center **29**, 10 (1961).

² C. B. Clark, Phys. Rev. **125**, 1898 (1962).

³ G. Leibfried, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. 7, Pt. 1, p. 104.

⁴ D. N. Singh and W. A. Bowers, Phys. Rev. **116**, 279 (1959).

⁵ J. de Launay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, p. 219.

one for very low temperatures, and to the central model at higher temperatures.) This model was used by Dayal and Sharan⁶ for computing the vibration spectrum and specific heat for lithium. They used theoretical elastic constants and determined the frequency spectrum by a method somewhat different from the one used here.

The next section of this paper concerns the computation of the frequency spectra histograms for the three models. The following section presents the method of computation of the specific heats and Debye characteristic temperatures for lithium and vanadium for each model. In the final section these results are compared with empirical data and results calculated by others.

For lithium, a comparison between calculated values of specific heat and low-temperature experimental values may not be meaningful. All the models described here are for bcc crystals. Martin,⁷ however, has shown that below about 80°K bcc lithium is transformed into the hcp form, with the proportions of the two forms depending upon the history of the sample.

THE VIBRATIONAL SPECTRA HISTOGRAMS

For a given model, one obtains the secular equation in the familiar harmonic approximation. The secular equation for the central model is given, for example, in the references cited in footnotes 1 and 5, and the latter contains the secular equation for the de Launay model. The secular equation for the noncentral model may be written in the form of a determinant equal to zero, where the elements of the determinant are

$$D_{ii} = (\alpha_1 + 2\alpha_3)(1 - C_1 C_2 C_3) + (3/2)\alpha_2 S_i^2 - 3M\omega^2/8, \quad (1)$$

$$D_{ij} = (\alpha_1 - \alpha_3)S_i S_j C_k, \quad i, j, k \text{ different}, \quad (2)$$

where i, j, k have the values 1, 2, or 3; ω is the frequency of the plane wave multiplied by 2π ; $C_i = \cos(k_i a/2)$; $S_i = \sin(k_i a/2)$; k_i is the i th component of the wave vector; α_1 is the nearest-neighbor radial force constant; α_2 is the next-nearest-neighbor force constant; α_3 is the nearest-neighbor angular force constant; M is the atomic mass; and a is the lattice constant. If $\alpha_3 = 0$, this model reduces to the central model.

In each of the three secular equations, it is convenient to perform some collections of terms and define a dimensionless quantity Ω by the relation $\Omega^2 = 3M\omega^2/8\alpha_1$.

The resulting secular equation then contains ratios involving the original force constants of the model. These ratios or elastic parameters (as well as the force constants themselves) can be related to the macroscopic elastic constants, c_{11} , c_{12} , c_{44} for cubic crystals. These relations for each model are

central model,

$$\beta = \alpha_2/\alpha_1 = (c_{11} - c_{12})/3c_{44}, \quad (3)$$

⁶ B. Dayal and B. Sharan, Proc. Roy. Soc. (London) **A259**, 361 (1960).

⁷ D. L. Martin, Proc. Roy. Soc. (London) **A254**, 444 (1960).

noncentral model,

$$\beta = \alpha_2/\alpha_1 = (c_{11} - c_{44})/(c_{12} + 2c_{44}), \quad (4)$$

$$\gamma = \alpha_3/\alpha_1 = (c_{44} - c_{12})/2(c_{12} + 2c_{44}),$$

de Launay's model,

$$\beta = \alpha_2/\alpha_1 = (c_{11} - c_{12})/3c_{44},$$

$$\zeta = (\alpha_1' - \alpha_1)/\alpha_1 = (c_{12} - c_{44})/3c_{44}, \quad (5)$$

$$\eta = (2\alpha_1' - 3\alpha_2') - (2\alpha_1 - 3\alpha_2) = 0.$$

The elastic constants for lithium were measured by Nash and Smith⁸ for the temperature 78°K. Those for vanadium were measured by Alers⁹ at temperatures ranging down to 4.2°K.

The symmetry of cubic lattices is such that only propagation vectors \mathbf{k} which lie in a region bounded by a trihedral solid angle of $(4\pi/48)$ sr, and the first Brillouin zone boundary, need be considered. For a bcc lattice this region of \mathbf{k} space is a tetrahedron with vertex at the origin. It is convenient to work with a dimensionless quantity \mathbf{K} which is related to the propagation vector \mathbf{k} by

$$\mathbf{K} = a\mathbf{k}/2\pi. \quad (6)$$

In \mathbf{K} space the corresponding tetrahedral region (called the basic tetrahedron) was taken to be that bounded by the planes

$$K_2 = 0, \quad K_1 = K_2, \quad K_1 = K_3, \quad \text{and} \quad K_1 + K_3 = 1. \quad (7)$$

The Univac 1103 electronic computer at the Southern Methodist University Computing Laboratory was used to calculate the three roots of the secular equation at each of 42 925 points within the basic tetrahedron in \mathbf{K} space. The solutions were classified as belonging to the proper one of 100 equal intervals between 0 and Ω_{\max} . A count was made of the number of solutions in each range. These numbers constitute the tabular histogram representing the frequency spectrum. Histograms were obtained in this manner for lithium and vanadium for each of the three models.¹⁰

THE SPECIFIC HEATS

As explained by Clark,¹¹ the choice of vectors \mathbf{K} for which the secular equation was solved caused the frequency spectra to be inaccurate at very low frequencies. In addition the increments of size $\Omega_{\max}/100$ were found

⁸ H. C. Nash and C. S. Smith, J. Phys. Chem. Solids **9**, 113 (1959).

⁹ G. A. Alers, Phys. Rev. **119**, 1532 (1960).

¹⁰ Tabular histograms and tables of the Debye Θ (calculated for the temperature range 1 to 600°K) for all three models of both lithium and vanadium have been deposited as Document No. 7476 with the American Documentation Institute (ADI) Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and remitting \$1.25 for photoprints, or \$1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

¹¹ C. B. Clark, J. Grad. Res. Center **30**, 15 (1962).

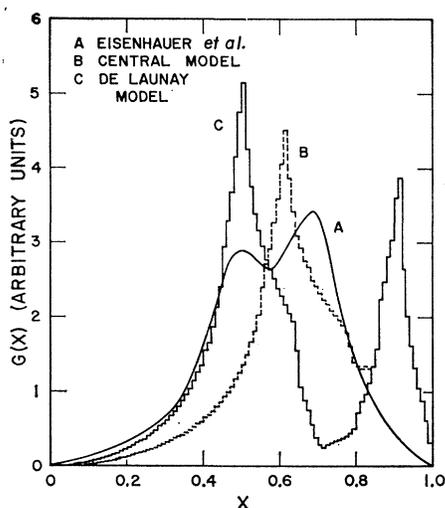


FIG. 1. Frequency spectra for vanadium. The dimensionless variable x is proportional to frequency. The smooth curve is based on neutron diffraction experiments by Eisenhauer *et al.* B is a portion of the spectrum calculated for the central model, while C was calculated for the de Launay model. Both calculations utilized elastic constant values determined by Alers.

too large for computing specific heats at very low temperatures. The histogram entries from the first n intervals were fitted according to the method of least squares by a polynomial curve having the form

$$f(x) = c_1x^2 + c_2x^4, \quad (7)$$

where $x = \Omega/\Omega_{\max}$. The values of n , c_1 , and c_2 for each model for both lithium and vanadium are given in Table I.

TABLE I. Parameters used to supplement histograms.

Element	Model	n	c_1	c_2
Li	central	13	7721.10	43 816.36
	noncentral	14	9622.39	7697.97
	de Launay	20	8179.43	92 771.29
V	central	18	3043.52	628.35
	noncentral	23	5728.76	1165.65
	de Launay	20	5764.97	2632.13

The formula for computation of the specific heat and a description of the program for determining values of the Debye characteristic temperature Θ were given in two previous papers.^{2,11} Values of the atomic heat at constant volume divided by three times the universal gas constant were calculated at 92 temperatures ranging from 1 to 600°K. Some of the corresponding values of Θ were used to prepare the graphs presented in the next section.

COMPARISONS

The vibration spectrum for lithium has been reported by Dayal and Sharan,⁶ for de Launay's model, but using different elastic constants than those used to obtain the

results found here. The Univac program was modified to repeat the calculations of Dayal and Sharan. Several errors in their reported values of frequencies were revealed. The principal one is that the maximum frequency occurs at the corner $(\frac{1}{2}, 0, \frac{1}{2})$ of the basic tetrahedron, rather than within the basic tetrahedron as their paper indicated.¹² The same paper lists values of specific heat at low temperatures, but their calculations suffer also from the difficulties which led us to introduce the polynomial fit for the low-frequency range and divide the intervals in Ω (or x) into smaller increments for the low-temperature calculations.

Eisenhauer *et al.*¹³ found the vibration spectrum of vanadium from neutron diffraction experiments. Figure 1 shows their curve together with the histogram obtained from de Launay's model, and the lower frequency peak in the histogram obtained from the central model. The higher frequency peaks for all three models are so nearly the same they cannot be shown conveniently on the same graph at the scale of Fig. 1. The lower peak for the noncentral model occurs at a slightly lower value of x than that for de Launay's model. To avoid further complicating the diagram it was not shown in Fig. 1.

As previously mentioned, Singh and Bowers⁴ used different elastic constants with the noncentral model to obtain the spectrum for vanadium. Figure 2 shows their histogram as well as that obtained in this work. The difference is striking, as would be expected from the difference in elastic constants.

The values of Θ at low temperatures have been calculated for the three models. The results for vanadium are

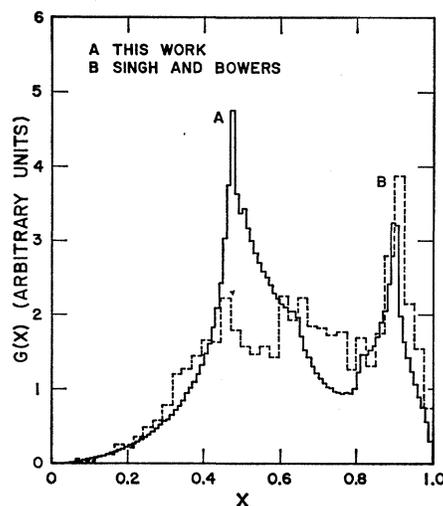


FIG. 2. Frequency spectra from the noncentral model for vanadium. The histogram A (solid line) utilized elastic constants determined by Alers. The histogram B (broken line) was determined by Singh and Bowers using quite different elastic constants.

¹² This has been acknowledged by B. Dayal (private communication).

¹³ C. M. Eisenhauer, I. Pelah, D. J. Hughes, and H. Palevsky, *Phys. Rev.* **109**, 1046 (1958).

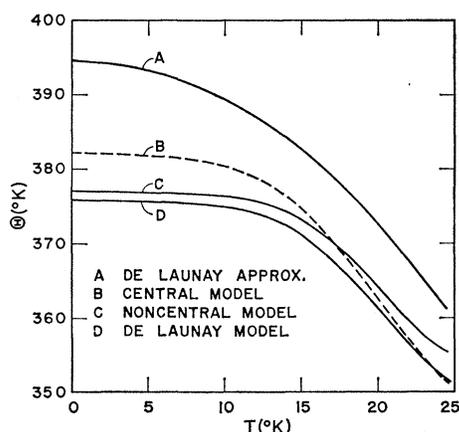


FIG. 3. Debye characteristic temperatures for vanadium. Curve A was determined by use of de Launay's tables for the central model; B is from the central model described in this paper; C is from the noncentral model; D is from the de Launay model. All four calculations utilized elastic constants determined by Alers.

shown in Fig. 3, along with a curve calculated from de Launay's tables⁵ for the central model. Actually the parameters for the latter had to be obtained by extrapolation of the values computed by de Launay, because the range of elastic constants considered by him did not include those for vanadium. The spread of values of the Debye characteristic temperature at 0°K, Θ_0 , among the three models amounts to 1 or 2% of Θ_0 . Alers⁹ reports a calculated value of 399.3°K for Θ_0 . Corak *et al.*¹⁴ reports a value of $338 \pm 5^\circ\text{K}$ based on experimental measurements of specific heat. It seems evident that none of these models adequately represents vanadium.

The results of calculations for Li are presented in Fig. 4 together with an empirical curve due to Roberts.¹⁵

¹⁴ W. S. Corak, B. B. Goodman, C. B. Satterthwaite, and A. Wexler, *Phys. Rev.* **102**, 656 (1956).

¹⁵ L. M. Roberts, *Proc. Phys. Soc. (London)* **B70**, 744 (1957).

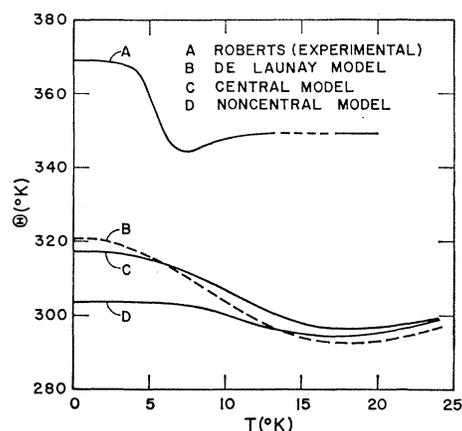


FIG. 4. Debye characteristic temperatures for lithium. Curve A was reported by Roberts from experimental data for specific heat. The other three represent results of calculations for the three models described in this paper; B is for the de Launay model; C is for the central model; D is for the noncentral model. All calculations utilized elastic constant values determined by Nash and Smith.

The spread in Θ_0 values due to the three models is greater than for vanadium. All, however, give considerably different values than those reported by Roberts. The models are all for bcc crystals. As pointed out by Martin,⁷ the measurements reported by Roberts may have been for samples in which a large part of the Li had undergone a transition to hcp form.

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