valleys such as

$$P(x,z)=\sum_{1}^{n}\cos(\nu x)e^{-\nu z}$$

reflects negative particles only up to a small value of energy, while positive ones are reflected up to much larger energies.

ACKNOWLEDGMENT

Many thanks are due to C. R. Buckey, who guided the author, a novice at the computer, with never-failing patience; who restored the author's self-respect when he lost again and again in arguments with the computer; and who wrote most of the more difficult passages in the programs.

PHYSICAL REVIEW VOLUME 164, NUMBER 3 15 DECEMBER 1967

Angular Forces in the Lattice Dynamics of Face-Centered Cubic Metals

P. S. YUEN AND Y. P. VARSHNI
Department of Physics, University of Ottawa, Ottawa, Canada
(Received 19 June 1967)

The lattice dynamics of the fcc lattice has been investigated using a model in which, in addition to central forces, interatomic forces include angular forces of the type employed by Clark, Gazis, and Wallis. The model has been applied to copper, and results are presented for dispersion curves, vibration spectra, and effective calorimetric and x-ray Debye temperatures.

INTRODUCTION

ANGULAR forces were introduced into lattice dynamics long ago by Born[1] in his treatment of the diamond lattice. However, there have been very few investigations bearing on the applicability or otherwise of the assumption of angular forces in metallic crystals.

Recently, Clark, Gazis, and Wallis[2] have investigated the frequency spectra of bcc lattices using a model in which, in addition to central forces, interatomic forces include angular forces of the type introduced by Gazis, Herman, and Wallis.[3] In the present paper the lattice dynamics of the fcc lattice has been investigated using such a model. An application has been made to copper, for which theoretical and experimental results are compared for dispersion curves, and effective calorimetric and x-ray Debye temperatures.

ANGULAR FORCE MODEL

We consider a monoatomic crystal lattice formed by $(N+1)$ particles. Each particle has a mass M. The potential energy V of the crystal may be expanded in a Taylor series.

In the following, we denote $(\partial^2 V/\partial u_m \partial v_n)_0$ by

$$V\begin{pmatrix}u & v\\ m & n\end{pmatrix};\quad \begin{pmatrix}u=x,y,z;\ v=x,y,z\\ m=0,\cdots,N;\ n=0,\cdots,N\end{pmatrix}.$$

The angular frequencies ω are obtained from the solution of the secular equation[4,5]

$$\left|\sum_n V\begin{pmatrix}u & v\\ 0 & n\end{pmatrix}e^{i2\pi\mathbf{k}\cdot\mathbf{R}_n}-\omega^2 M\delta_{uv}\right|=0, \tag{1}$$

where $\mathbf{R}_n$ is the equilibrium position of the particle n.

For the fcc lattice, we denote the position of a lattice point by

$$\mathbf{R}_{0n}=\mathbf{R}_n=\tfrac{1}{2}a\mathbf{N}_n, \tag{2}$$

where a is the length of one side of the cube. In this notation, (1) becomes

$$\left|\sum_n V\begin{pmatrix}u & v\\ 0 & n\end{pmatrix}e^{i\mathbf{p}\cdot\mathbf{N}_n}-\omega^2 M\delta_{uv}\right|=0, \tag{3}$$

where

$$\mathbf{p}=\pi a\mathbf{k}.$$

The model that we are considering employs central forces between a particle and each of its first and second neighbors, as well as angular forces which depend on the changes of angles in the triangles formed by the particle and its first and second neighbors. This type of angular force has been used by Clark *et al.*[2] The effects of the more distant neighbors are neglected.

Since we only need to use terms of $(\partial^2 V/\partial u_0 \partial v_n)_0$, we can treat the potential energy due to the central force interaction and the angular force interaction separately.

[1] M. Born, Ann. Physik **44**, 605 (1914).
[2] B. C. Clark, D. C. Gazis, and R. F. Wallis, Phys. Rev. **134**, A1486 (1964).
[3] D. C. Gazis, R. Herman, and R. F. Wallis, Phys. Rev. **119**, 533 (1960).
[4] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1962).
[5] R. A. Smith, *Wave Mechanics of Crystalline Solids*, (Chapman and Hall Ltd., London, 1961).

A. Central Force Interaction

If α_1 and α_2 denote the force constant for first and second neighbors, respectively, we have the well-known results

$$\sum_n V_\alpha \begin{pmatrix} x & y \\ 0 & n \end{pmatrix} e^{i\mathbf{p}\cdot\mathbf{N}_n} = 2\alpha_1 S_1 S_2, \tag{4}$$

and

$$\sum_n V_\alpha \begin{pmatrix} x & x \\ 0 & n \end{pmatrix} e^{i\mathbf{p}\cdot\mathbf{N}_n} = 4\alpha_1 - 2\alpha_1 C_1(C_2+C_3) + 4\alpha_2 S_1^2, \tag{5}$$

where

$$C_j = \cos\pi a k_j, \quad S_j = \sin\pi a k_j, \tag{6}$$

and k_1, k_2, and k_3 are components of $\mathbf{k}$ in Cartesian coordinates. Other terms can be obtained by circular permutations of the indices.

B. Angular Force Interaction

Before considering the fcc lattice, we first discuss the angular force interaction in general terms.

There are two types of triangles in which we are interested. One is formed by a particle and two of its first neighbors, called type (1) triangles. The other is formed by a particle, one of its first neighbors, and one of its second neighbors, called type (2) triangles.

The changes in the angles of a triangle are obtained by comparing the triangle of the equilibrium positions of these particles with the projection of the triangle of these particles onto the plane of their equilibrium positions.

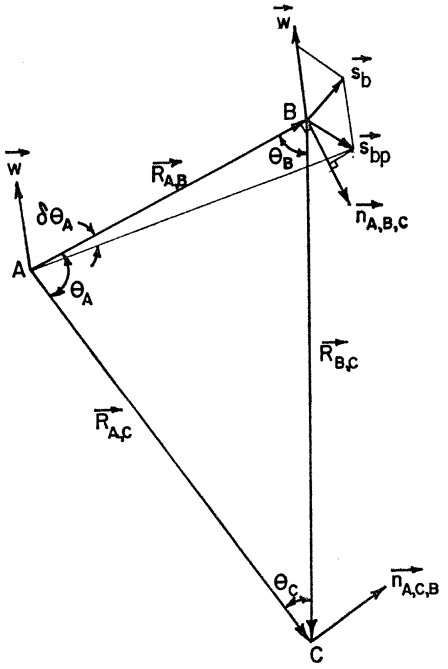


FIG. 1. Angular force.

Consider the triangle formed by three particles a, b, and c (see Fig. 1). Let A, B, and C denote their equilibrium positions; $\mathbf{s}_a$, $\mathbf{s}_b$, and $\mathbf{s}_c$ their small displacements. $\mathbf{n}_{A,B,C}$ is defined as a unit vector which is in the plane A, B, C and normal to the vector $\mathbf{R}_{A,B}$. We are dealing with the angle θ_A at A. The convention for the direction of $\mathbf{n}_{A,B,C}$ is that, when $\mathbf{n}_{A,B,C}$ is applied to the particle B it reduces the angle θ_A. (From definition, $\mathbf{n}_{A,B,C} \equiv \mathbf{n}_{B,A,C}$.) $\mathbf{R}_{A,B}$ is the position vector of B relative to A, and $R_{A,B} = |\mathbf{R}_{A,B}|$.

$\mathbf{w}$ denotes a unit vector normal to the plane A, B, C in a direction such that $\mathbf{R}_{A,C}$, $\mathbf{R}_{A,B}$, and $\mathbf{w}$ form a right-handed system. The projection of the displacement $\mathbf{s}_b$ on the plane A, B, C is

$$\mathbf{s}_{bp} = (\mathbf{w}\times\mathbf{s}_b)\times\mathbf{w}. \tag{7}$$

Since the displacement s_b is small in magnitude, the effective change in the angle θ_A (as far as the angular force is concerned) due to s_b is given by

$$-\frac{\mathbf{s}_{bp}\cdot\mathbf{n}_{A,B,C}}{R_{A,B}} = -\frac{\mathbf{s}_b\cdot\mathbf{n}_{A,B,C}}{R_{A,B}}. \tag{8}$$

The change in the angle θ_A due to the displacements $\mathbf{s}_a$, $\mathbf{s}_b$, and $\mathbf{s}_c$ is

$$\delta\theta_A = \frac{(\mathbf{s}_a-\mathbf{s}_b)\cdot\mathbf{n}_{A,B,C}}{R_{A,B}} + \frac{(\mathbf{s}_a-\mathbf{s}_c)\cdot n_{A,C,B}}{R_{A,C}}. \tag{9}$$

The change in the potential energy due to $\delta\theta_A$ is given by

$$\tfrac{1}{2}\kappa(\delta\theta_A)^2, \tag{10}$$

where κ is the angular force constant associated with the angle θ_A.

For the case of the fcc lattice, the two types of triangles are shown in Fig. 2. The first one is that formed by a particle and two of its first neighbors which are

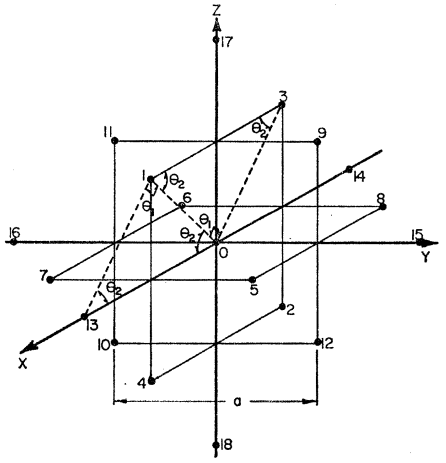


FIG. 2. The first and second neighbors of the particle 0 of the fcc lattice.

both in the same plane of the coordinate axes. They are triangles equivalent to Δ0, 1, 3 in Fig. 2; particles 1 and 3 are both in the X-0-Z plane. This type of triangle is called type (1).

The other type is formed by a particle, one of its first neighbors, and one of its second neighbors. They are triangles equivalent to Δ0, 1, 13; particle 13 is a first neighbor of particle 1. This type of triangle is called type (2).

There are, in all, 12 type (1) triangles and 24 type (2) triangles, with reference to the particle 0. As shown in Fig. 2, all 36 triangles are identical and each is isosceles with two equal angles θ_2; $\theta_2=45°$. We shall associate with each angle $\theta_1(\theta_1=90°)$ in the triangles an angular force constant κ_1, and each angle θ_2 an angular force constant κ_2.

After carrying out the lengthy derivations we finally

TABLE I. The lattice constant a, the elastic constants c_{11}, c_{12}, c_{44}, and the longitudinal-phonon frequency at the zone boundary in the [100] direction ν_b of copper.

Temp. (°K)	a (10^{-8} cm)	c_{11}	c_{12}	c_{44}	Reference	[100]ν_b (10^{12} cps)
		10^{11} dyn/cm				
0	3.6029[a]	17.62	12.494	8.177	[c]	7.43[d]
100	3.6045[a]	17.493	12.425	8.059	[c]	7.41[d]
200	3.6093[a]	17.192	12.295	7.816	[c]	7.36[d]
300	3.6147[b]	16.839	12.142	7.539	[c]	7.3[e]

[a] Calculated from the room-temperature value by the method of R. J. Corruccini and J. J. Gniewek, Natl. Bur. Std. (U. S.) Monograph **29**, 4 (1961).
[b] *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1963), 2nd ed.
[c] W. C. Overton Jr. and J. Gaffney, Phys. Rev. **98**, 969 (1955).
[d] Derived from the experimental value at 300°K as explained in the text.
[e] See Refs. 6 and 8.

obtain the following results:

$$\sum_n V_{\kappa_1}\begin{pmatrix} x & y \\ 0 & n \end{pmatrix} e^{i\mathbf{p}\cdot\mathbf{N}_n} = -\frac{16\kappa_1}{a^2} S_1 S_2, \tag{11}$$

$$\sum_n V_{\kappa_1}\begin{pmatrix} x & x \\ 0 & n \end{pmatrix} e^{i\mathbf{p}\cdot\mathbf{N}_n} = \frac{32\kappa_1}{a^2} - \frac{16\kappa_1}{a^2} C_1(C_2+C_3) - \frac{4\kappa_1}{a^2} \times (2\cos 2\pi a k_1 - \cos 2\pi a k_2 - \cos 2\pi a k_3), \tag{12}$$

$$\sum_n V_{\kappa_2}\begin{pmatrix} x & y \\ 0 & n \end{pmatrix} e^{i\mathbf{p}\cdot\mathbf{N}_n} = 0, \tag{13}$$

$$\sum V_{\kappa_2}\begin{pmatrix} x & x \\ 0 & n \end{pmatrix} e^{i\mathbf{p}\cdot\mathbf{N}_n} = \frac{32\kappa_2}{a^2} - \frac{16\kappa_2}{a^2} C_1(C_2+C_3). \tag{14}$$

Equation (3) may be written in the form

$$|D(\mathbf{q}) - \omega^2 M I| = 0, \tag{15}$$

where I is the 3×3 unit matrix. The elements of the dynamical matrix $D(q)$, obtained by combining the various terms, are as follows:

$$D_{xx} = 2[\alpha_1 + (8/a^2)(\kappa_1+\kappa_2)][2 - C_1(C_2+C_3)] + 4\alpha_2 S_1^2 - \frac{4\kappa_1}{a^2} \times (2\cos 2\pi a k_1 - \cos 2\pi a k_2 - \cos 2\pi a k_3), \tag{16}$$

$$D_{xy} = \left(2\alpha_1 - \frac{16\kappa_1}{a^2}\right) S_1 S_2. \tag{17}$$

Other terms can be obtained by circular permutations of the indices.

We determine the four force constants in terms of the three elastic constants and the longitudinal-phonon frequency ν_b in the [100] direction at the Brillouin zone boundary, given by

$$\nu_b = (1/\pi)\{(2/M)[\alpha_1 + (8/a^2)(\kappa_1+\kappa_2)]\}^{1/2}. \tag{18}$$

The resulting expressions are as follows:

$$\alpha_1 = \tfrac{1}{2}a(c_{12}-c_{44}) + \tfrac{1}{2}\pi^2\nu_b^2 M, \tag{19}$$

$$\alpha_2 = \tfrac{1}{4}a(c_{11}+2c_{44}) - \tfrac{1}{2}\pi^2\nu_b^2 M, \tag{20}$$

$$\kappa_1/a^2 = -\tfrac{1}{8}ac_{44} + \tfrac{1}{16}\pi^2\nu_b^2 M, \tag{21}$$

$$\kappa_2/a^2 = -\tfrac{1}{16}a(c_{12}-3c_{44}) - \tfrac{1}{16}\pi^2\nu_b^2 M. \tag{22}$$

TABLE II. Force constants for copper at different temperatures. All values are in the units of 10^3 dyn/cm.

Temp.	α_1	α_2	κ_1/a^2	κ_2/a^2
0	36.52	1.859	−0.090	−0.882
100	36.46	1.70	−0.0577	−0.926
200	36.29	1.415	−0.0009	−1.009
300	36.06	1.098	0.0617	−1.102

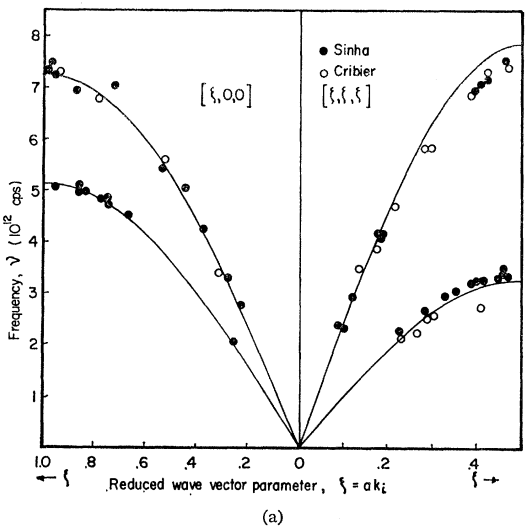
APPLICATION TO COPPER

The above model was applied to copper and calculations were carried out in the quasiharmonic approximation at four temperatures, viz., 0, 100, 200, and 300°K. The experimental data used in obtaining the force constants are tabulated in Table I. The dispersion curves have been measured only at 300°K; to obtain the longitudinal phonon frequency at the zone boundary in the [100] direction at other temperatures, the following approximation was employed:

$$\frac{\nu_b(T°)}{\nu_b(300°)} = \left[\frac{c_{11}(T)a^3(T)}{c_{11}(300)a^3(300)}\right]^{1/2}. \tag{23}$$

The force constants calculated from Eqs. (19) to (22) are shown in Table II. The dispersion curves were calculated from the 300°K data and are compared with the experimental results in Figs. 3(a) and 3(b).

The vibrational frequency distributions $g(\nu)$ were obtained at the four temperatures by calculating the frequencies at 1686 points in the irreducible 1/48 of



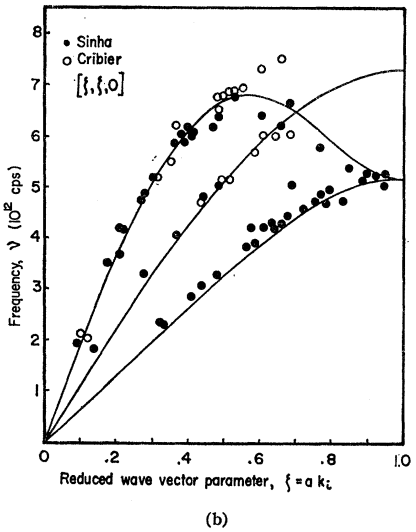


FIG. 3. (a) and (b): The dispersion curves of copper at 300°K. The curves shown are theoretical ones obtained from the angular-force model. Experimental points: ● (Ref. 6), ○ (Ref. 7).

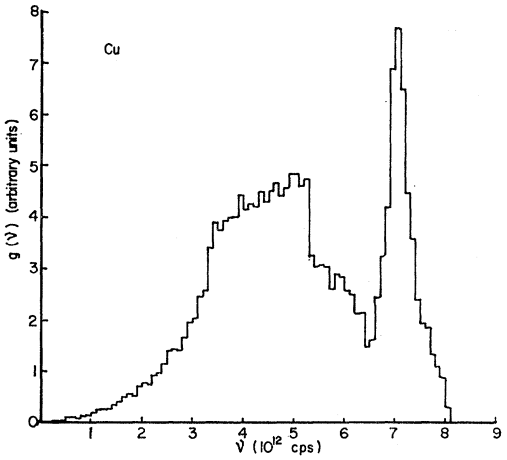


FIG. 4. The frequency spectrum histogram of copper at 0°K obtained by the angular force model.

the Brillouin zone; this gave a total of 192 000 frequencies. The histogram for $g(\nu)$ at 0°K is shown in Fig. 4.

The calculated effective calorimetric (Θ_D) and x-ray (Θ_M) Debye temperatures are shown in Figs. 5 and 6, respectively, together with experimental points. The theoretical curves are composite ones obtained from frequency distributions at the four temperatures.

DISCUSSION

The force constants show a very regular behavior with temperature. α_1 and α_2 decrease smoothly with increase in temperature; (κ_1/a^2) starts with a negative value at 0°K, becomes almost zero at 200°K, and takes a positive value at 300°K. The absolute value of (κ_2/a^2) increases with temperature. The magnitude of κ_2 is substantially greater than that of κ_1, which is almost

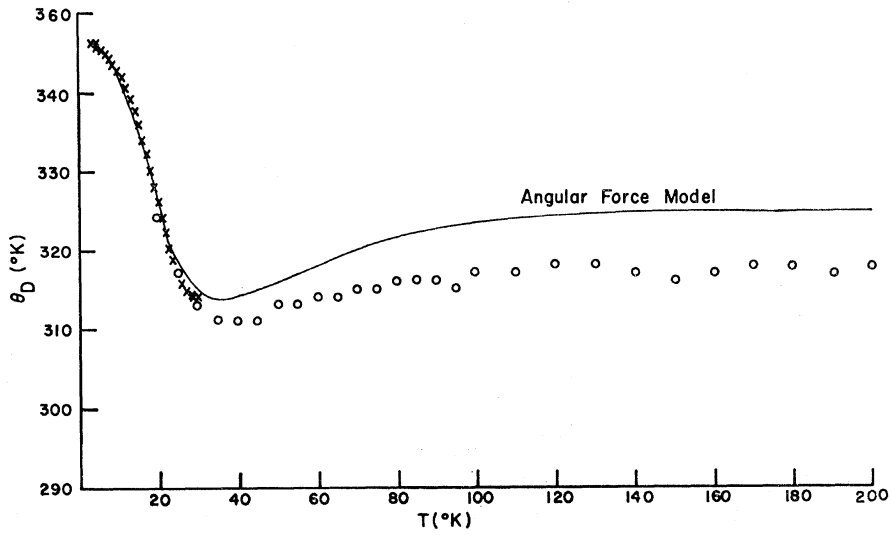


FIG. 5. Calculated and experimental calorimetric Debye Θ_D's of copper. Experimental points: × (Ref. 10), ○ (Ref. 9).

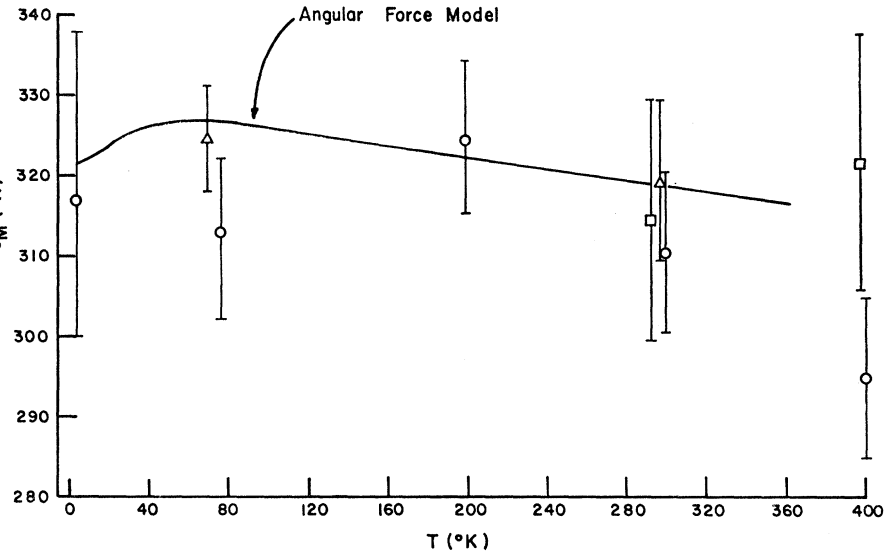


FIG. 6. Θ_M for copper. Solid line shows the theoretical curve. Experimental points: ○ [P. A. Flinn, G. M. McManus, and J. A. Rayne, Phys. Rev. **123**, 809 (1961)]; □ [E. A. Owen and R. W. Williams, Proc. Roy. Soc. (London) **A188**, 509 (1947), as quoted in T. H. K. Barron, M. L. Klein, A. J. Leadbetter, J. A. Morrison, and L. S. Salter, in *Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962*, edited by R. O. Davies (Butterworths Scientific Publications Ltd., London, 1963), p. 415.]; △ [D. R. Chipman and A. Paskin, J. Appl. Phys. **30**, 1992, 1998 (1959), as quoted above in Barron *et al.*].

negligible. A calculation for aluminum and nickel showed that the smallness of κ_1 is not a general result; for these two metals κ_1 and κ_2 are of the same order of magnitude.

The calculated dispersion curves [Figs. 3(a), 3(b)] are seen to be in good agreement with experimental points in all three directions. The experimental values shown in the diagrams are due to Sinha[6] and to Cribier *et al.*[7] Very similar results have been obtained recently by Svensson, Brockhouse, and Rowe[8] using a different method.

The frequency spectrum obtained here is very similar to that obtained by Sinha[6] from a sixth-neighbor force-constant model and that obtained by Svensson *et al.*,[8] also from a sixth-neighbor force-constant model but with one constraint among fifth-neighbor force constants.

The theoretical curve for the calorimetric Debye temperature is in very good agreement with the experimental values at low temperatures (Fig. 5), but lies slightly above the experimental points at medium temperatures. The experimental points are due to Martin.[9,10]

There are large uncertainties in the experimental values of x-ray Debye temperatures; the theoretical curve appears to be reasonably satisfactory. We may note that the decreasing trend of Θ_M at high temperatures is obtained only under a quasiharmonic approximation.

ACKNOWLEDGMENTS

The authors are thankful to Dr. J. A. Morrison for helpful discussions, and to the National Research Council of Canada for financial support.

[6] S. K. Sinha, Phys. Rev. **143**, 422 (1966).
[7] D. Cribier, B. Jacrot, and D. Saint-James, in *Proceedings of the International Atomic Energy Agency Symposium on Inelastic Scattering of Neutrons in Solids and Liquids, Vienna, October, 1960* (International Atomic Energy Agency, 1961); p. 549.
[8] E. C. Svensson, B. N. Brockhouse, and J. M. Rowe, Phys. Rev. **155**, 619 (1967).
[9] D. L. Martin, Can. J. Phys. **38**, 17 (1960).
[10] D. L. Martin, Phys. Rev. **141**, 576 (1966).