Frequency Spectra of Body-Centered Cubic Lattices*

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A Born-von Karman model has been used to determine the frequency spectrum for a body-centered cubic lattice. The model used contains noncentral angular stiffness forces as well as central forces between nearest and next-nearest neighbors. Frequency distributions have been calculated for vanadium and compared with experimental frequency distributions available from slow neutron experiments. Qualitative agreement was found between the shapes of the experimental and theoretical distributions. The calculated maximum frequency for vanadium was within 2% of that derived from the experimental frequency distribution. Dispersion curves for iron were also calculated, and were found to be in good agreement with experiment.

INTRODUCTION

THE frequency distribution of a body-centered cubic lattice of identical particles has been investigated using the Born-von Karman model of a crystal lattice. The interatomic forces used include noncentral forces of the type introduced by Gazis, Herman, and Wallis[1] in treating surface waves in a simple cubic crystal. These noncentral forces arise from the resistance to deformation of certain angles formed by three lattice points. Also included are central forces between nearest and next-nearest neighbors. Noncentral forces have been employed in recent calculations by Hendricks, Riser, and Clark,[2] which appeared after our work was essentially complete; however, the noncentral forces considered by them are different from those used here.

One of the primary aims of the investigation was to examine the effect of the inclusion of noncentral forces on the frequency distribution. Comparison between the central-force model and the model employed here was made for iron and for vanadium which is one of the more anisotropic body-centered cubic crystals. The central-force calculations for vanadium were available from the work of Clark.[3] The calculations with vanadium were also compared with the frequency distributions obtained by the slow neutron experiments of Stewart and Brockhouse,[4] and Eisenhauer *et al.*[5] Dispersion curves along specified directions were calculated for iron and compared with the experimentally determined dispersion curves of Low.[6]

LATTICE EQUATIONS OF MOTION

Although the equations of motion for central forces appear elsewhere, for example, in DeLaunay,[7] they will be repeated here in order to provide a continuity of notation. Taking a displacement vector with components u, v, and w in the x, y, and z directions, respectively, the force in the x direction on atom (j, m, n) due to the central-force interactions of nearest neighbors is given by

$$F_{x1}=\alpha[U-8u_{j,m,n}+V+W], \tag{1}$$

where

$$\begin{aligned}U=&(u_{j+1,m+1,n+1}+u_{j+1,m+1,n-1}+u_{j+1,m-1,n+1}\\&+u_{j+1,m-1,n-1}+u_{j-1,m+1,n+1}+u_{j-1,m+1,n-1}\\&+u_{j-1,m-1,n+1}+u_{j-1,n-1,m-1}),\\V=&(v_{j+1,m+1,n+1}+v_{j+1,m+1,n-1}-v_{j+1,m-1,n+1}\\&-v_{j+1,m-1,n-1}-v_{j-1,m+1,n+1}-v_{j-1,m+1,n-1}\\&+v_{j-1,m-1,n+1}+v_{j-1,m-1,n-1}),\\W=&(w_{j+1,m+1,n+1}-w_{j+1,m+1,n-1}+w_{j+1,m-1,n+1}\\&-w_{j+1,m-1,n-1}-w_{j-1,m+1,n+1}+w_{j-1,m+1,n-1}\\&-w_{j-1,m-1,n+1}+w_{j-1,m-1,n-1}),\end{aligned} \tag{2}$$

where α is the nearest-neighbor force constant. Similarly, the central-force interaction between next-nearest neighbors gives rise to a force on the atom (j,m,n) in the x direction given by

$$F_{x2}=\beta[u_{j+2,m,n}+u_{j-2,m,n}-2u_{j,m,n}], \tag{3}$$

where β is the next-nearest-neighbor force constant.

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

[6] G. G. E. Low, Proc. Phys. Soc. (London) **79**, 479 (1962).

[7] J. DeLaunay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2.

For the noncentral forces examined here it is assumed that a change in angle is related to a change in potential energy by a Hooke's law force constant. If V is the potential energy and $\delta\phi$ a change in angle, one obtains

$$V=\tfrac{1}{2}\gamma(\delta\phi)^2, \tag{4}$$

where γ is the force constant. In this treatment two general types of angles were considered; 36 angles of the type ϕ_1 in Fig. 1 associated with a force constant γ_1, and 72 angles of the type ϕ_2 in Fig. 1 associated with a force constant γ_2. The expansion of the potential energy is quite tedious but straightforward, and the total contribution from the angles considered results in a force on the atom of interest, in the x direction, given by

$$\begin{aligned}F_{x3}=&\gamma_1[-20u_{j,m,n}+2U-V-W+4(u_{j+2,m,n}+u_{j-2,m,n})\\&-(u_{j,m+2,n}+u_{j,m-2,n}+u_{j,m,n+2}+u_{j,m,n-2})]\\&-\gamma_2[-30u_{j,m,n}+3U+\tfrac{3}{2}(V+W)\\&+\tfrac{3}{2}(u_{j,m+2,n}+u_{j,m-2,n}+u_{j,m,n+2}+u_{j,m,n-2})],\end{aligned} \tag{5}$$

where U, V, and W are given by Eq. (2). These noncentral forces are invariant under rigid-body rotations.

The equation for the force in the x direction on the atom (j,m,n) due to the central and noncentral forces considered here may now be written as

$$\begin{aligned}F_x=&m\ddot{u}_{j,m,n}\\=&-u_{j,m,n}[8\alpha+2\beta+20\gamma_1+30\gamma_2]\\&+(\beta+4\gamma_1)(u_{j+2,m,n}+u_{j-2,m,n})+(-\gamma_1+\tfrac{3}{2}\gamma_2)\\&\times(u_{j,m+2,n}+u_{j,m-2,n}+u_{j,m,n+2}+u_{j,m,n-2})\\&+U(\alpha+2\gamma_1+3\gamma_2)+(V+W)(\alpha-\gamma_1+\tfrac{3}{2}\gamma_2),\end{aligned} \tag{6}$$

where U, V, and W are given as in Eq. (5). The forces in the y and z directions on the central atom are found by a circular permutation of u, v, and w, as well as the increments of their indices j, m, n.

SOLUTION OF THE EQUATIONS OF MOTION

The solutions of the equations of motion are assumed to be plane waves, where the usual cyclic boundary conditions of Born[8] are applied. The solutions for the motion of, say the nth, atom are written as

$$\begin{aligned}u_n&=X\exp 2\pi i(\nu t+\mathbf{k}\cdot\mathbf{r}_n),\\v_n&=Y\exp 2\pi i(\nu t+\mathbf{k}\cdot\mathbf{r}_n),\\w_n&=Z\exp 2\pi i(\nu t+\mathbf{k}\cdot\mathbf{r}_n).\end{aligned}$$

Here X, Y, and Z are the components of the plane-wave amplitude, and $\mathbf{k}$ is a propagation vector in the reciprocal lattice whose magnitude is the reciprocal of the wavelength. The values of $\mathbf{k}$ are restricted to the first Brillouin zone, as discussed by Brillouin.[9] Substitution of these solutions into the equations of motion gives three homogeneous linear equations in X, Y, and Z.

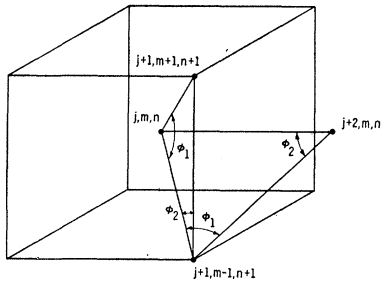

FIG. 1. Body-centered cubic lattice showing primitive (ϕ_1) and secondary (ϕ_2) angles.

A nontrivial solution requires that the determinant of the coefficients of X, Y, and Z vanish. This condition yields the secular equation

$$\begin{vmatrix}A_1-m\omega^2 & B & C\\ B & A_2-m\omega^2 & D\\ C & D & A_3-m\omega^2\end{vmatrix}=0, \tag{7}$$

where

$$\begin{aligned}A_i=&(8\alpha+16\gamma_1+24\gamma_2)(1-\cos\Phi_1\cos\Phi_2\cos\Phi_3)\\&+4\beta\sin^2\Phi_i-2\gamma_1(5\cos 2\Phi_i-\cos 2\Phi_1-\cos 2\Phi_2\\&-\cos 2\Phi_3-2)+3\gamma_2(2+\cos 2\Phi_i-\cos 2\Phi_1\\&-\cos 2\Phi_2-\cos 2\Phi_3),\end{aligned} \tag{8}$$

$$B=8(\alpha-\gamma_1+\tfrac{3}{2}\gamma_2)\cos\Phi_3\sin\Phi_1\sin\Phi_2,$$

$$C=8(\alpha-\gamma_1+\tfrac{3}{2}\gamma_2)\cos\Phi_2\sin\Phi_1\sin\Phi_3,$$

$$D=8(\alpha-\gamma_1+\tfrac{3}{2}\gamma_2)\cos\Phi_1\sin\Phi_2\sin\Phi_3.$$

In Eq. (8), $\Phi_i=\pi ak_i$ $(i=1,2,3)$ where a is the distance between next-nearest neighbors for the body-centered cubic lattice.

Symmetry considerations allow a restriction of the values of Φ_i to points within 1/48 of the first Brillouin zone. The limits on the Φ_i are then given by $0\leq\Phi_1\leq\frac{1}{2}\pi$, $0\leq\Phi_2\leq\frac{1}{2}\pi$, and $0\leq\Phi_3\leq\pi$. This reduces the values of Φ_i to those within the region in Φ space bounded by the planes $\Phi_1=\Phi_2$, $\Phi_2=0$, $\Phi_1=\Phi_3$ and $\Phi_1+\Phi_3=\pi$.

For a cubic equation of the type resulting from the expansion of Eq. (7) Blackman[10] has shown that maxima in $m\omega^2$ can occur only when Φ_1, Φ_2, Φ_3 have some combination of the values 0, $\frac{1}{2}\pi$, π. The point $\Phi_1=\Phi_2=\Phi_3=0$ is excluded as $m\omega^2=0$ at this point. Substitution of those values of Φ_1, Φ_2, Φ_3 which are within the first 1/48 Brillouin zone showed that in most cases considered the maximum occurs at $(\frac{1}{2}\pi, 0, \frac{1}{2}\pi)$. This maximum frequency may be found directly from Eq. (7) and is

$$m\omega_{\max}{}^2=4(4\alpha+\beta+5\gamma_1)+42\gamma_2. \tag{9}$$

It was found in actual calculations that the position of the maximum could be shifted to $(0,0,\pi)$ when certain values of the elastic constants, such as those for sodium, given by Quimby and Siegell,[11] were assumed. In this case the maximum frequency is given by

$$m\omega_{\max}{}^2=16(\alpha+2\gamma_1+3\gamma_2). \tag{9a}$$

[8] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954).
[9] L. Brillouin, *Wave Propagation in Periodic Structures* (Dover Publications, New York, 1953).
[10] M. Blackman, Proc. Roy. Soc. (London) **A148**, 365 (1935).
[11] S. L. Quimby and S. Siegell, Phys. Rev. **54**, 293 (1938).

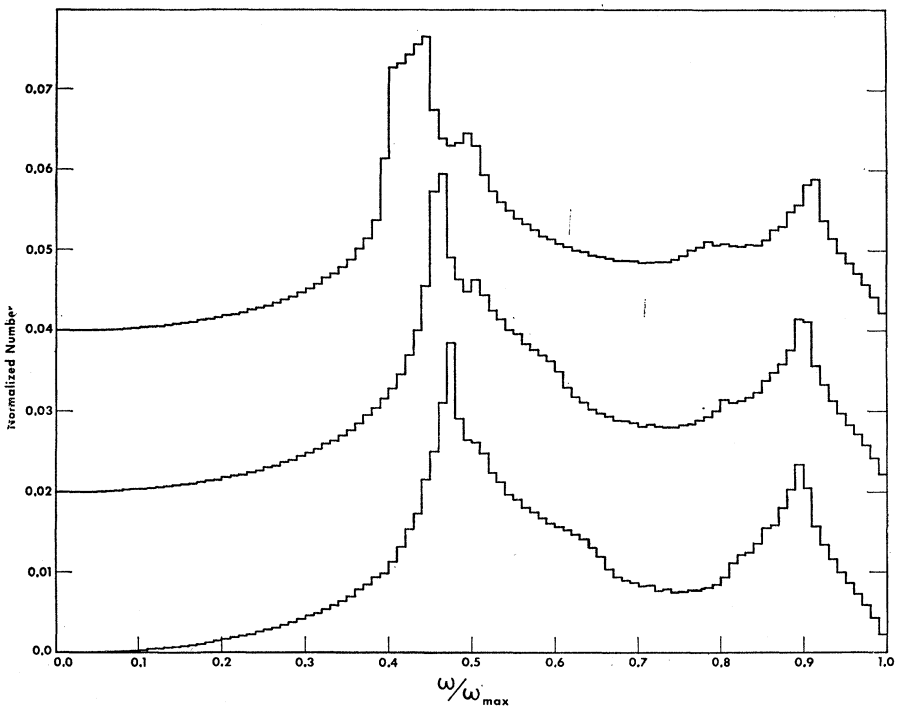

FIG. 2. Three calculated frequency histograms for vanadium with $\gamma_2/\gamma_1=0.0$ (upper curve), $\gamma_2/\gamma_1=0.5$ (middle curve), and $\gamma_2/\gamma_1=1.0$ (bottom curve). *Note:* For display purposes, while the scale of the ordinate is the same for all three curves, the origin for the middle curve is at 0.02 and is at 0.04 for the upper curve.

RELATIONSHIPS BETWEEN ELASTIC CONSTANTS AND LATTICE FORCE CONSTANTS

In the limit of long wavelengths, when the wavelength is much greater than the lattice spacing, the plane waves are effectively propagating as in a continuous medium. This allows the identification of the lattice force constants with the elastic constants of the medium found from measurements of the velocity of sound. These relationships are obtained by expanding the displacement components such as $u_{j+p,m+q,n+r}$ in a Taylor series about $u_{j,m,n}$, substituting into the equation of motion and matching the coefficients of the second order derivatives with those of the continuum equations of motion. The results are:

$$\begin{aligned} ac_{11}&=2(\alpha+\beta+6\gamma_1+3\gamma_2),\\ ac_{12}&=2(\alpha-3\gamma_1+\tfrac{3}{2}\gamma_2),\\ ac_{44}&=2(\alpha+\gamma_1+\tfrac{9}{2}\gamma_2). \end{aligned} \tag{10}$$

If $\gamma_2=0$, the above three equations determine the lattice force constants uniquely; otherwise, the force constants are determined assuming, for example, a given ratio of γ_2/γ_1. The value γ_2/γ_1 is used as a parameter in the sequel. The elastic constants for vanadium are those of Alers.[12] It may be observed that the maximum frequency when it occurs at $(\frac{1}{2}\pi,0,\frac{1}{2}\pi)$, as is usual, is a function of the elastic constants only and is

$$m\omega_{\max}{}^2=2a(c_{12}+2c_{44}+c_{11}). \tag{11}$$

However, when the maximum frequency occurs elsewhere it is also a function of γ_2/γ_1.

[12] G. A. Alers, Phys. Rev. **119**, 1532 (1960).

CALCULATION OF THE FREQUENCY DISTRIBUTION

In order to obtain the true distribution of frequencies in a macroscopic crystal Eq. (7) would have to be solved for a very large number of points within the first Brillouin zone, equal to the number of degrees of freedom of the particles in the crystal. A systematic method was used for choosing a relatively small number of solution points within the first zone. It is assumed that solution points are uniformly distributed such that an allowed point exists within a volume element in Φ space, and further that the frequencies at all points within the element are equal to the value of the frequency at the center of the element. The values of Φ_i were chosen in a regular manner by stepping along the axes in intervals of 0.01π. Thus the volume elements were cubes of volume $10^{-6}\ \pi^3$.

Some of the solution points were on the bounding planes and were not, of course, centers of a cube lying entirely within the first Brillouin zone. There was some question of the desirability of including these points without properly weighing their contribution to the frequency distribution in the first zone. A numerical investigation of the most extreme case, that of the frequency distribution obtained with all points on the bounding planes included with the same weight as the interior points, showed that the resulting frequency distribution was essentially the same as the distribution with no boundary points included. Due to this result only points in the interior of the first 1/48th Brillouin zone were finally chosen. These considerations resulted in the inclusion of approximately 39 000 solution points in the 1/48th zone. Histograms representing the

frequency distribution were prepared from the calculated frequencies by finding the number of frequencies contained in a given frequency interval. The frequency interval chosen was 1.0% of the maximum frequency.

The cubic equation for the square of the frequency was solved using the Cardan method to find the first root, and the remaining quadratic to find the other two roots. A check on the accuracy of this method of calculating the frequency showed that six figures of accuracy were present for most cases. In the case of two equal roots the accuracy could be reduced to five figures; however, an error of this magnitude is not significant in the construction of the frequency histogram. The calculations were performed on an IBM-7090 computer.

RESULTS

The elastic constants for vanadium at 300°K are given by Alers[12] as

$$c_{11}=22.795\times10^{11}\text{ dyne-cm}^{-2},$$
$$c_{12}=11.870\times10^{11}\text{ dyne-cm}^{-2},$$
$$c_{44}=4.255\times10^{11}\text{ dyne-cm}^{-2}.$$

The maximum frequency calculated from Eq. (11), using these elastic constants, is 8.87×10^{12} cps which compares well with the experimental value of 9×10^{12} cps extrapolated from the curve given by Eisenhauer.[5] The two constant central-force model gives a maximum frequency of 7.07×10^{12} cps. Thus the three constant model gives a better result for the maximum frequency. The calculated and experimental frequency distributions are, however, quite different with regard to the location of the two major peaks, with the calculated frequency distribution having more widely spread maxima. The parameter γ_2/γ_1 may be varied without destroying the good agreement with the experimental maximum frequency. Figure 2 shows the frequency historgrams for vanadium for ratios of γ_2/γ_1 of 0.5 and 1.0, along with the case for $\gamma_2=0$. Figure 2 indicates that increasing the ratio of γ_2/γ_1 reduces the intensity of the first peak and moves the two maxima closer together producing better agreement with experiment. In view of those results, the frequency histogram for $\gamma_2/\gamma_1=1.5$ was also calculated and a smoothed curve obtained from these results is shown in Fig. 3 together with the experimental curve of Eisenhauer. For comparison the smoothed curve for the central-force model of Clark is also presented.

To indicate the effect that an uncertainty regarding the elastic constants might play in the determination

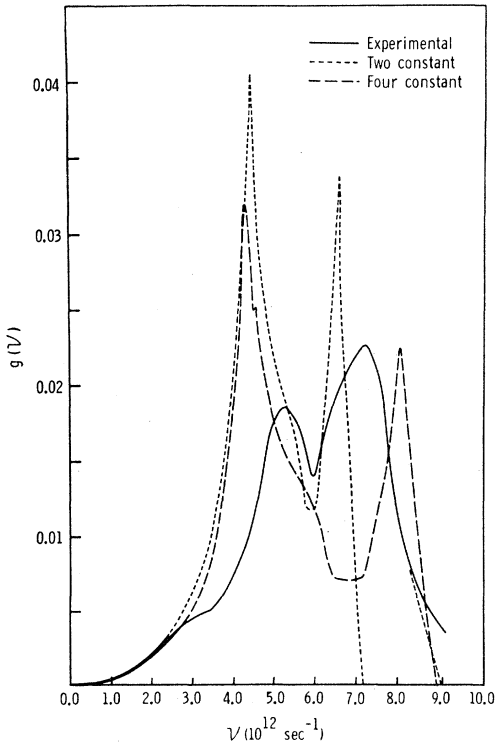

FIG. 3. The experimental results of Eisenhauer presented with the frequency distribution of Clark and the model used here with $\gamma_2/\gamma_1=1.5$. The results are normalized such that the area under the curves are the same.

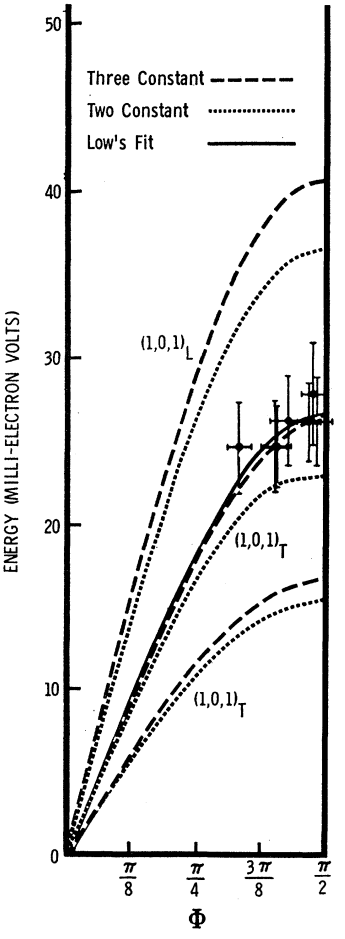

FIG. 4. Dispersion curves for iron along the [101] direction, $\Phi_1=\Phi_3=\Phi$, $\Phi_2=0$ where $\Phi_1=\pi ak_1$, along with the experimental results of Low, and Low's best fit.

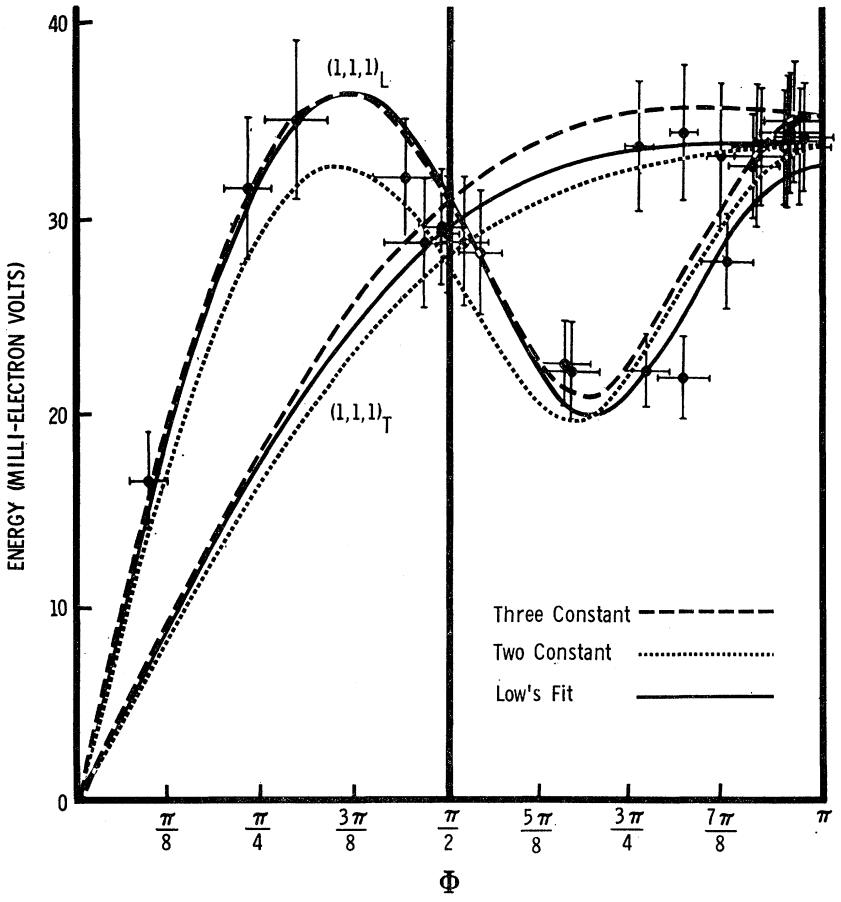

FIG. 5. Dispersion curves for iron along the [111] direction, $\Phi_1=\Phi_2=\Phi_3=\Phi$, where $\Phi_1=\pi a k_1$ along with the experimental results of Low, and Low's best fit.

of the frequency distribution, vanadium distributions were calculated using elastic constants varied by $\pm 10\%$ independently and assuming $\gamma_2=0$. Briefly, it was noted that increasing c_{12} and c_{11} by 10% tends to spread the peaks while increasing c_{44} brings the maxima together slightly. It was also apparent that increasing c_{11} and c_{44} by 10% increased the sharpness of the low-frequency peak while increasing c_{12} had the opposite effect. None of these frequency distributions seem to fit the experimental one appreciably better than the distribution with the unchanged elastic constants, and the calculated maximum frequencies are all in the neighborhood of the experimental maximum.

In addition to the frequency spectra discussed above, the model was used to calculate frequency dispersion curves. The calculations were compared with dispersion curves for iron as determined by Low.[6] Using the elastic constants given by Low for iron at 16°C as

$$c_{11}=2.332\times10^{12}\ \text{dyne-cm}^{-2},$$
$$c_{12}=1.355\times10^{12}\ \text{dyne-cm}^{-2},$$
$$c_{44}=1.180\times10^{12}\ \text{dyne-cm}^{-2},$$

dispersion curves were calculated along the [101], [111], and [001] directions. For comparison the same calculations were performed using a two-constant central-force model. The results of these calculations are shown in Figs. 4–6 along with the experimental results of Low. These calculations showed that the maximum frequency of 9.735×10^{12} cps for the three-constant model was higher than the maximum frequency of 8.711×10^{12} cps found for the two-constant model. Comparison with Low's curves shows that the three-constant model matches the experiment better than the two-constant model; however, both are, in general, well within the experimental error. The results of the three-constant model within the first zone, are essentially indistinguishable from the fit to the experimental data given by Low. The largest discrepancies occur for dispersion curves along the [111] direction, and even here the difference is apparent only for values of Φ outside the first zone. The inclusion of the angular stiffness terms has, in general, improved the agreement with experiment in this case.

CONCLUSION

The dynamical properties of a body-centered cubic lattice of identical particles have been investigated using the Born-von Karman model of a crystal lattice. The model employed contained noncentral as well as

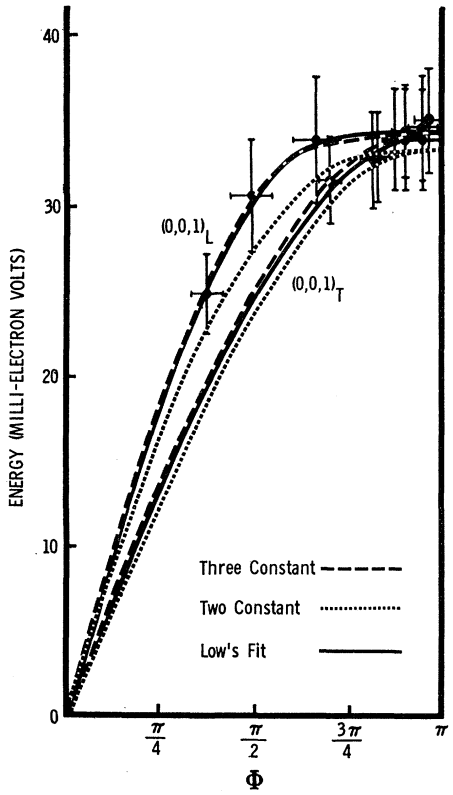

FIG. 6. Dispersion curves for iron along the [001] direction, $\Phi_1=\Phi_2=0$, where $\Phi_3=\pi a k_3$, along with the experimental results of Low, and Low's best fit.

central forces, namely, noncentral angular stiffness forces and central forces between nearest and next-nearest neighbors.

Frequency distribution histograms have been constructed for vanadium and compared with the experimental frequency distributions available from slow neutron experiments. The calculated maximum frequency for vanadium was in good agreement with that derived from the experimental frequency distributions, an improvement over the results of the central-force model. Our model containing a single angular stiffness interaction ($\gamma_2/\gamma_1=0$) gives a frequency distribution which is very similar to that obtained by Hendricks *et al.*[2] with their noncentral model. Both distributions yield a separation between the two major peaks which is significantly larger than that found experimentally. Inclusion of a second angular stiffness interaction into our model ($\gamma_2/\gamma_1\neq 0$) gives a small improvement but not enough to produce agreement with experiment. The disagreement in the experimental and theoretical values of the separation between the two major peaks in the frequency distribution might possibly be removed by including additional interactions in the model. It may well be; however, that short-range forces are inadequate, and that long-range forces are required. Since vanadium is a metal, the effects of the electron gas may be significant as discussed by DeLaunay.[7] The recent calculation of Hendricks, Riser, and Clark,[2] however, indicates that the use of DeLaunay's model does not resolve this difficulty. Failure of the adiabatic approximation in a metal might also be a factor which should be taken into account.

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