so that

$$G(\theta,\varphi)=(2\pi i/w_0)\{1-\beta_0P_2(\cos\theta)\}^{-1}$$
$$\times\Big\{[\sigma-k\cos\psi+i(a^2+k^2\sin^2\psi)^{\frac{1}{2}}]^{-3}$$
$$\times\Big[1+\Big(1+\frac{\sigma-k\cos\psi+i(a^2+k^2\sin^2\psi)^{\frac{1}{2}}}{\sigma}\Big)$$
$$\times\Big(\frac{k^2}{\sigma^2}\Big)\Big(\frac{1-\beta_0P_2(\cos\Theta)}{1-\beta_0P_2(\cos\theta)}\Big)\Big]\Big\}_{\sigma=k\cos\psi+i(a^2+k^2\sin^2\psi)^{\frac{1}{2}}}$$
$$=-\frac{\pi}{4w_0}\frac{(a^2+k^2\sin^2\psi)^{-\frac{3}{2}}}{[1-\beta_0P_2(\cos\theta)]}$$
$$\times\Big[1+\frac{[k\cos\psi+3i(a^2+k^2\sin^2\psi)^{\frac{1}{2}}]k^2\{1-\beta_0P_2(\cos\Theta)\}}{[k\cos\psi+i(a^2+k^2\sin^2\psi)^{\frac{1}{2}}]^3\{1-\beta_0P_2(\cos\theta)\}}\Big]. \quad (17b)$$

We expand in terms of k, i.e.,

$$G(\theta,\varphi)=\mathfrak{A}(\theta,\varphi)+k\mathfrak{B}(\theta,\varphi)+k^2\mathfrak{C}(\theta,\varphi)+\cdots, \quad (18b)$$

where

$$\mathfrak{A}(\theta,\varphi)=-(\pi/4w_0a^3)\{1-\beta_0P_2(\cos\theta)\}^{-1},$$
$$\mathfrak{B}(\theta,\varphi)=0,$$
$$\mathfrak{C}(\theta,\varphi)=(3\pi/4w_0a^5)\{1-\beta_0P_2(\cos\Theta)\}\{1-\beta_0P_2(\cos\theta)\}^{-2}+(3\pi/8w_0a^5)\times\sin^2\psi\{1-\beta_0P_2(\cos\theta)\}^{-1}. \quad (19b)$$

The integral $I(\mathbf{k})$ can now be written as in Eq. (63). In this expression

$$I_0=-\frac{\pi}{4w_0a^3}\int_0^{\pi}\frac{d\theta\sin\theta}{1-\beta_0P_2(\cos\theta)}\int_0^{2\pi}d\varphi$$
$$=-(\pi^2/w_0a^3)g, \quad (20b)$$

g being given by Eq. (66). Also

$$I_1=\frac{3\pi}{4w_0a^5}[1-\beta_0P_2(\cos\Theta)]\int_0^{\pi}\frac{d\theta\sin\theta}{[1-\beta_0P_2(\cos\theta)]^2}\int_0^{2\pi}d\varphi$$
$$+\frac{3\pi}{8w_0a^5}\int_0^{\pi}\frac{d\theta\sin\theta}{1-\beta_0P_2(\cos\theta)}\int_0^{2\pi}d\varphi$$
$$\times\{1-[\cos\Theta\cos\theta+\sin\Theta\sin\theta\cos(\varphi-\Phi)]^2\}$$
$$=\frac{3\pi^2}{2w_0a^5}[1-\beta_0P_2(\cos\Theta)]\int_{-1}^{1}[1-\beta_0P_2(\mu)]^{-2}d\mu$$
$$+\frac{\pi^2}{2w_0a^5}\int_{-1}^{1}\Big(\frac{1-P_2(\cos\Theta)P_2(\mu)}{1-\beta_0P_2(\mu)}\Big)d\mu. \quad (21b)$$

Making use of the fact that

$$\int_{-1}^{1}[1-\beta_0P_2(\mu)]^{-2}d\mu=\Big(\frac{2}{2+\beta_0}\Big)\Big[\frac{1}{1-\beta_0}+g\Big], \quad (22b)$$
$$\int_{-1}^{1}\Big(\frac{1-P_2(\cos\Theta)P_2(\mu)}{1-\beta_0P_2(\mu)}\Big)d\mu$$
$$=2g-\Big(\frac{2}{\beta_0}\Big)(g-1)P_2(\cos\Theta), \quad (23b)$$

we obtain Eq. (65).

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Low-Temperature Behavior and Dispersion Relations of Face-Centered Cubic Metals

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The temperature variation of the effective Debye temperature Θ near the absolute zero is investigated for some face-centered cubic metals on the basis of: (a) the Born and Begbie noncentral force theory taking nearest neighbor interactions only into account; (b) the customary central force model, used by Fine, Leighton, etc. The results are found to be qualitatively similar to those recently obtained by Bhatia and Horton on the basis of a model for monovalent metals proposed by Bhatia. Our results are based throughout on Houston's approximation to the frequency spectrum.

The dispersion relations for Cu are calculated along the (100), (110), and (111) directions on the basis of (a), with nearest and next-nearest neighbor interactions; on the basis of (b); and from the equations of Bhatia and Horton. The results are compared with recent experimental results obtained from temperature-diffuse x-ray scattering by Jacobsen. It is found that, with a choice of force constants consistent with the observed elastic constants, all three theories agree with the experimental results to about the same extent.

1. INTRODUCTION

IN two recent papers[1,2] a model for monovalent cubic metals for obtaining the secular equation determining the normal modes of vibration was proposed and applied to the calculation of the frequency spectra and specific heats of Na and Ag. The main purpose of the model put forward in I was to take into account explicitly the volume-dependent forces in a metal in some approximate way. Alternatively, we have available the following two other methods

[1] A. B. Bhatia, Phys. Rev. **97**, 363 (1955); we shall employ the notation of this paper and refer to it as I.
[2] A. B. Bhatia and G. K. Horton, Phys. Rev. **98**, 1715 (1955). This paper will be subsequently referred to as II.

of calculating frequency spectra and specific heats of metals:

(i) We may use the central force model taking into account nearest and next-nearest neighbor interactions only. This gives two force constants. The three elastic constants for a cubic metal, however, do not, in general, satisfy Cauchy's relations. Hence one first substracts from them a contribution which depends on the volume only (supposedly due to the free electrons and not affecting the lattice frequencies) and assumes that the remaining constants obey the Cauchy relations.[3] The force constants are then determined in the usual manner by comparing the expressions for the velocities of long-wavelength disturbances in terms of the force constants and the elastic constants. This model has been used by several authors.[4]

(ii) Born and Begbie[5] start with a general noncentral interaction potential function between the ions. For a monovalent face-centered cubic lattice, this procedure gives three force constants for nearest neighbor forces, two for next to nearest neighbors, and four for third-nearest neighbors. If one confines oneself to nearest neighbors only, the three force constants may be determined from the experimental values of the three elastic constants.[6] So far as is known to us, no calculations of frequency spectra and specific heats have been made on this simple model.[7]

Attempts, however, have been made to determine the dispersion (frequency—wave number) relations for certain directions of propagation from the temperature-dependent diffuse scattering of x-rays from which the force constants may be determined. Jacobsen[8] has recently carried out such an analysis for Cu. He retained terms up to, and including, third-nearest neighbors in the theory of Born and Begie and determined the nine force constants thus available by obtaining a best fit between the experimental and theoretical dispersion curves along the (100), (110), and (111) directions with the aid of the Massachusetts Institute of Technology Whirlwind I electronic computer. The over-all fit so obtained was within a few percent. He then determined the elastic constants from the force constants and found that the values of one of the elastic constants, namely c_{44}, differed substantially (15%) from that obtained by Gaffney and Overton[9] by the ultrasonic method.

In this paper we made a comparative study of some of the results that may be derived from the above-mentioned three theories. In Sec. 2 we examine the temperature dependence of the effective Debye Θ near the absolute zero of temperature for some face-centered cubic metals on the basis of the central force model and the Born and Begbie theory with only nearest neighbor interactions for the latter. These results are then compared with those obtained in II. Our work is based exclusively on Houston's approximation to the frequency spectrum.

In Sec. 3, we calculate the dispersion relations for Cu along the (100), (110), and (111) directions on the three theories and compare them with the experimental results of Jacobsen. In calculating these relations from the Born and Begbie theory, we have taken into account nearest the next-nearest neighbor interactions only. We thus have five force constants. However, unlike Jacobsen, we impose three subsidiary conditions on them, namely, that the values of the three elastic constants, determined from the force constants by going to the long-wavelength limit, take on the experimental values found by the ultrasonic method. This leaves us with only two independent force constants at our disposal. If such a procedure is adopted and terms involving up to third-nearest neighbor interactions are retained, one would have six force constants at one's disposal. The effect of including these extra terms on our results is also discussed briefly.

Our conclusions are discussed at the ends of Secs. 2 and 3.

2. LOW-TEMPERATURE BEHAVIOR OF THE EFFECTIVE DEBYE Θ

(a) Theory

The low-temperature behavior of the effective Debye Θ was discussed in II on the basis of the secular equation derived in I, by means of Houston's method and an expansion of the frequency spectrum in powers of the frequency ω. Since only even powers of ω occur in such an expansion, this is equivalent to an expansion of Θ in even powers of the temperature; the first two terms in this expansion were retained and the results given for representative face-centered and body-centered cubic metals.

[3] P. C. Fine, Phys. Rev. **56**, 355 (1939) who, to our knowledge, was the first to suggest this advice following results on the elastic constants of cubic metals by K. Fuchs, Proc. Roy. Soc. (London) **A153**, 622 (1935); **157**, 444 (1936).

[4] P. C. Fine, reference 3; R. B. Leighton, Revs. Modern Phys. **20**, 165 (1948); E. Bauer, Phys. Rev. **92**, 58 (1953), and others.

[5] M. Born and G. H. Begbie, Proc. Roy. Soc. (London) **A188**, 179 (1947). The following comment on the general theory of Born and Begbie, may be made here: The expressions for the elastic constants are related to certain sums, over the ions of the second derivatives of the potential function. As noticed by K. Huang, Proc. Roy. Soc. (London) **A203**, 179 (1950), the symmetry relations (2.28) of Born and Begbie do not hold for a general interaction potential function; in fact it may be shown that (2.28) necessarily lead to Cauchy's relations. We wish to point out, however, that their matrix equation (2.30), connecting explicitly the elastic constants with the elements of the dynamical matrix, is correct and leads to the same expressions for the elastic constants as given by Huang. Of course, Born and Begbie in their work implicitly assume certain conditions (discussed by Huang) which must be satisfied in order that the results of the atomic theory go over into those of the elasticity theory in the long wave limit. We are indebted to Dr. Bhatia for this comment.

[6] This procedure is not possible for body-centered or simple cubic lattices, for then one has either too few force constants (with nearest neighbors only), or too many (with nearest and next-nearest neighbors).

[7] Such calculations are in progress at this University.

[8] E. H. Jacobsen, Phys. Rev. **97**, 654 (1955). References to other work of a similar nature may be found in this paper.

[9] J. Gaffney and W. C. Overton, Phys. Rev. **95**, 602 (1954).

We have carried out an analogous study for the central force theory and for the theory of Born and Begbie[6] in which the nearest neighbor interactions only were retained. In this way a unique identification of the force constants in terms of the elastic constants was possible. The details of the analysis were given in II and will not be reproduced here. Using the same notation as in II, our results may be summarized as follows. The equivalent Debye temperature Θ_T at temperature T is given by

$$\Theta_T=\Theta_0[1-(20\pi^2/21)(\alpha_2/\alpha_1)(\kappa T/\hbar)^2+\ldots], \quad (1)$$

where

$$\Theta_0=(9N_0/\alpha_1)^{\frac{1}{3}}\hbar/\kappa, \quad (2)$$

and α_1 and α_2 are directly connected with the force constants, and hence the elastic constants, of the crystal.

Using room-temperature values of the elastic constants, the quantities α_1 and α_2 may be evaluated. Our results are summarized in Table I.

It can be shown that α_1 is always positive while α_2 may be negative. In the central force theory, as in the theory of Bhatia (when the small longitudinal contributions are neglected), one finds a critical value of $\sigma(=\epsilon/c_{44}=[c_{11}-c_{12}-2c_{44}]/c_{44})$, on which Θ_T, defined in (1), depends, for which the Θ_T is initially flat, to be -1.39. In the theory of Born and Begbie, while α_2 can again be negative, the Θ_T does not depend on the elastic constants through σ alone and so we cannot ascribe a critical value to σ for which α_2 changes sign.

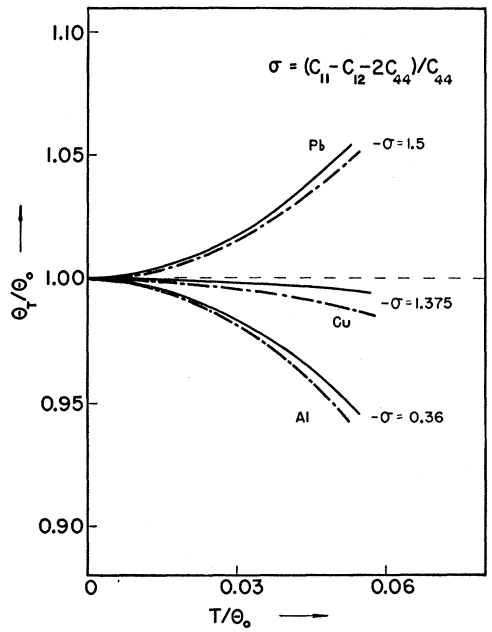

FIG. 1. Comparison of the Born and Begbie noncentral force theory (solid curve) and the central force theory (broken curve) predictions for the low-temperature Debye Θ_T. These curves are based on results obtained by Houston's method.

TABLE I. Comparison of the three theories considered in this paper concerning their prediction of the value of the coefficient $(T/\Theta_0)^2$ in the expansion of the characteristic Debye temperature.

Metal	$-\sigma=-\epsilon/c_{44}$	Θ_0	$(20\pi^2/21)(\alpha_2/\alpha_1)(\kappa\Theta_0/\hbar)^2$ Born and Begbie	Bhatia	Central force
Al	0.36[a]	408	18.3	24.2	21.0
Ag	1.31	205	7.23	7.28	7.85
Cu	1.375	320	1.65	1.25	4.08
Pb	1.5	83	−19.6	−17.5	−17.5

[a] This value is quoted incorrectly in part II.

(b) Discussion

It is clear from Table I and the corresponding Fig. 1 that all three theories discussed above yield values for Θ_T/Θ_0 that differ, for small T/Θ, by a few percent. For instance, for Pb, both the noncentral force *and* the central force theories yield a maximum in the Θ_T-T curve before the usual minimum. Our results are, therefore, at variance with those of Leighton[10] who predicts a curve for Pb that corresponds more closely to our curve for Al. We are unable to resolve this discrepancy because we have used different approximations to the frequency spectrum.

We note that the results in Table I are based on room temperature values of the elastic constants. For the theory of Bhatia and the central force theory,[11] the change to absolute zero elastic constants causes a negligible change in Θ_T/Θ_0, as was already pointed out in part II for Cu. For the Born and Begbie theory, the coefficient 1.65 would be increased by about 0.8. Thus the general features of our results are unchanged by the use of absolute-zero elastic constants.

In view of the close agreement found for all three theories, it would be most interesting to have an experimental study made of the temperature variation of the effective Debye Θ at low temperatures, especially for Pb. For Pb the experiments would presumably have to be done in the presence of a magnetic field to avoid the effects due to superconductivity.

[10] See reference 4. We note that Table III and Eqs. (8) in Leighton's paper are not consistent for small λ and that this point may be connected with the divergence in our results. A systematic improvement of Houston's method is being carried out at this University and will be applied to Ag to resolve this discrepancy. We note that the values of Θ_0, which depend only on α_1 derived by a slightly different application of Houston's method by A. B. Bhatia and G. E. Tauber [Phys. Mag. **45**, 1211 (1954)], were correct to a few percent. [There is a misprint in this article in that the right hand side of (5) should be multiplied by $\rho^{\frac{1}{3}}$, where ρ is the density of the crystal.] The longitudinal contributions to α_1 and α_2 were ignored in II.

[11] The central force theory discussed in this work is a nearest and next-nearest neighbor theory. The theory of Bhatia, on the other hand, takes only nearest neighbors into account. A rough calculation shows that neglecting next-nearest neighbor forces in the central force theory or including them in the Bhatia theory causes significant changes in the dispersion curves.

3. DISPERSION RELATIONS

(a) Theory

In this section we shall need the solutions of the secular equation determining the angular frequencies ω of the elastic waves in a face-centered cubic metal for $\mathbf{k}$ vectors lying along the three principal directions of a cubic metal; namely the (100), (110), and the (111) directions. For the theory of Bhatia, these solutions have already been given in II. In the noncentral force theory of Born and Begbie, the secular equation may be readily solved along these three directions in $\mathbf{k}$ space and we find

100 Direction

$$\left.\begin{aligned} L:&\quad \omega^2=(8/\rho a^2)\sin^2(ak/2\sqrt{2})\\ &\qquad\times[c_{11}-\alpha\sin^2(ak/2\sqrt{2})],\\ T_1\}\ T_2\}:&\quad \omega^2=(8/\rho a^2)\sin^2(ak/2\sqrt{2})\\ &\qquad\times[c_{44}-\beta\sin^2(ak/2\sqrt{2})]. \end{aligned}\right\}\quad(3)$$

110 Direction

$$\left.\begin{aligned} L:&\quad \omega^2=(8/\rho a^2)\sin^2(ak/4)\\ &\qquad\times[2c_{11}-\epsilon-(2c_{11}-c_{44}-\epsilon+\beta)\sin^2(ak/4)],\\ T_1:&\quad \omega^2=(8/\rho a^2)\sin^2(ak/4)\\ &\qquad\times[\epsilon+2c_{44}-(c_{44}+\epsilon+\beta)\sin^2(ak/4)],\\ T_2:&\quad \omega^2=(8/\rho a^2)\sin^2(ak/4)\\ &\qquad\times[2c_{44}-(2c_{44}-c_{11}+\alpha)\sin^2(ak/4)]. \end{aligned}\right\}\quad(4)$$

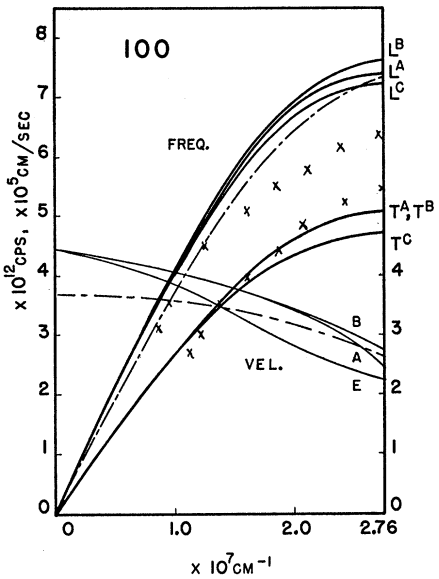

FIG. 2. Frequency and velocity *versus* wave vector for longitudinal and traverse elastic waves propagating in the (100) direction in copper. The broken curve represents the central force theory while the curves labeled A represents the theory of Bhatia. The curves labeled B represent the Born and Begbie theory with nearest neighbor force constants only, while those labeled C were computed from the Born and Begbie theory with $\alpha=1.5\times10$ in. dynes/cm^2 and $\beta=1\times10$ in. dynes/cm^2. Curve E is the velocity curve corresponding to the best-fit experimental longitudinal frequency curve of Jacobsen, whose experimental points are shown as crosses.

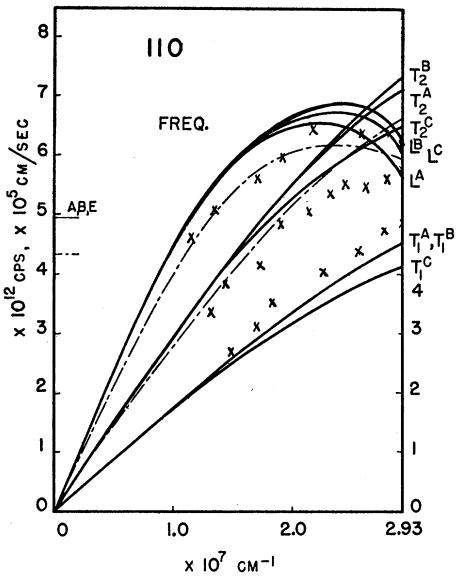

FIG. 3. Frequency *versus* wave vector for longitudinal and transverse elastic waves propagating in the (110) direction in copper. Jacobsen's experimental results are shown as crosses. Curves are labeled successively, with A standing for the theory of Bhatia, B for the theory of Born and Begbie with $\alpha=\beta=0$, and C for the theory of Born and Begbie with $\alpha=1.5\times10$ in. dynes/cm^2 and $\beta=1\times10$ in. dynes/cm^2. The velocity labeled A, B, and E corresponds to the initial value of the velocity predicted by the theory of Bhatia, the theory of Born and Begbie, and the experiments, while the broken line gives the initial velocity according to the central force theory.

111 Direction

$$\left.\begin{aligned} L:&\quad \omega^2=(2/\rho a^2)(3c_{11}-2\epsilon)\sin^2(ak/\sqrt{6}),\\ T_1\}\ T_2\}:&\quad \omega^2=(2/\rho a^2)(3c_{44}+\epsilon)\sin^2(ak/\sqrt{6}). \end{aligned}\right\}\quad(5)$$

α and β are proportional to the next to nearest neighbor force constants. The symbols L and T refer to the three (longitudinal and transverse) branches. All other symbols have their usual meaning as in II. We have imposed the subsidiary conditions that the five force constants must lead to the correct ultrasonic elastic constants c_{11}, c_{12}, and c_{44}. The dispersion relations for the central force theory may be obtained from those of the Born and Begbie theory in the usual manner.

The dispersion relations for Cu for the three theories, with two sets of values for α and β in the Born and Begbie theory, are plotted in Figs. 2, 3, and 4 together with the experimental results of Jacobsen.

(b) Discussion

Jacobsen was able to fit his experimental dispersion curves very closely by using the Born and Begbie theory, retaining up to and including third-nearest neighbor forces. As he showed in his Table I, this close fit was achieved at the expense of the correct value for c_{44}. Now it has been shown in II that Θ_T is much more sensitive to changes in c_{44} and $c_{11}-c_{12}$

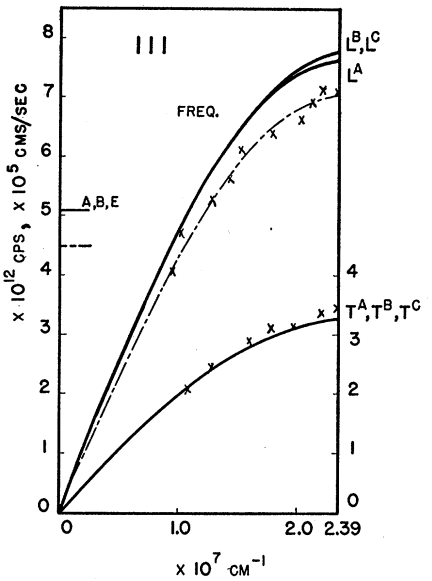

FIG. 4. Frequency *versus* wave vector for longitudinal and transverse elastic wave propagating in the (111) direction in copper. Jacobsen's experimental results are shown as crosses. Curves are labeled successively, with A standing for the theory of Bhatia, B for the theory of Born and Begbie with $\alpha=\beta=0$, and C for the theory of Born and Begbie with $\alpha=1.5\times10$ in. dynes/cm^2 and $\beta=1\times10$ in. dynes/cm^2. The velocity labeled A, B, and E corresponds to the initial value of the velocity predicted by the theory of Bhatia, the theory of Born and Begbie, and the experiments, while the broken curve gives the initial velocity according to the central force theory.

than in c_{11} and c_{12}. Thus a change of 10% in the value of c_{44} (and $c_{11}-c_{12}$) caused a similar percentage change in the value of Θ_T at 20°K. Now the results of Figs. 2 to 4 show a similar sensitivity by the dispersion curves. With our subsidiary conditions removing three of the force constants to give the correct elastic constants, the dispersion relations according to the born and Begbie theory with nearest and next-nearest neighbor forces no longer fit Jacobsen's experimental curves any more closely than do those of the Bhatia or central force theories. A choice of α and β that is different from zero, curves with superscript C, does not help because (i) to cause a significant change in the dispersion curves would now require unreasonably large values of the second-nearest neighbor force constants; (ii) improved agreement with experiments for one branch in a certain direction clearly means worse agreement elsewhere. We have also made a rough calculation including third-nearest neighbor forces and it appears that our conclusions are not materially altered. We note that in the (111) direction the dispersion relations are independent of the second-nearest neighbor force constants.

We conclude with a remark concerning the phase velocities given in Fig. 2. Curve E corresponds to the experimental results of Jacobsen while curves A, B, and the broken curve are the predictions respectively of the Bhatia, Born and Begbie, and central force theories. It is clear that in the first half of the range, the noncentral theories, and in particular the Bhatia theory, give much better agreement with experiment than the central force theory which in turn is somewhat better at the medium wavelengths. At the upper end of the frequency spectrum, all theories predict roughly the same result. We have only given the longitudinal velocities in the (100) direction because these results are quite typical for the other two directions. For the transverse waves, the correspondence between all theories and the experiments is very much closer. In the (100) and (111) directions we do, however, give the initial values of the noncentral force theories and the experimental curve on the one hand and the central force theory on the other. In this way we bring out the considerable divergence between the central force curve and the others at low frequencies, a fact not clearly brought out by the dispersion curves.

Thus, to summarize, it may be noted that the Bhatia and central force theories give results which are not too different from each other and are somewhat closer to Jacobsen's experimental dispersion curves than the Born and Begbie theory with our subsidiary conditions. However, since the experimental results of Jacobsen have a probable error of 10%, it appears to be somewhat premature to discuss these differences.

We would like to thank Dr. A. B. Bhatia for many valuable discussions.

Note added in Proof.—In a recent paper, C. B. Walker [Phys. Rev. **103**, 547 (1956)] has carried out an x-ray study of the lattice vibrations in Al analogous to the work of Jacobsen for Cu. The comments we have made on Jacobsen's results on Cu are equally applicable to Walker's results on Al.

We would also like to make the following general remark. The applicability to metals of the Born and Begbie theory, which does not completely include the effect of the conduction electrons, is very much an open question. Under these circumstances we feel it would be of interest to have an x-ray study made of a substance for which the theory is known, such as solid argon or NaCl, where the assumptions of the central force theory are obeyed.