field and two sub-bands of the $3d$ shell also having spins parallel and antiparallel.

It appears that the resistivities of these materials also can be understood on the basis of the same four-band model. Actually only the resistivity of Ni as a function of temperature has been worked out in detail but this had appeared, at the outset, to be the most doubtful case.

Since all of the calculations have used the saturation magnetization data to determine the number of carriers in each band, the saturation magnetization data is also consistent with this model.

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Elastic Spectrum of Copper from Temperature-Diffuse Scattering of X-Rays*

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Measurements have been made of the temperature-diffuse scattering of x-rays from a single crystal of copper at 300°K by using crystal monochromated Cu $K\alpha$ radiation. The measurements were analyzed by the method of Laval and James to give dispersion curves of frequency *vs* wave vector for longitudinal and transverse waves in the 100, 110, and 111 directions. These results were then expressed in terms of the generalized force constants of the Born theory of lattice dynamics.

By considering the interaction of first, second, and third neighbors, nine force constants are involved, and these have been evaluated from the dispersion curves. These force constants appear in the secular equation of frequency *vs* wave vector and constitute the necessary data for computing a complete vibrational frequency spectrum.

Such a spectrum has been calculated from the secular equation, by machine computation, for 3417 wave vectors. From this spectrum a specific heat curve was calculated and compared with experiment in the range of 15°K to 100°K.

I. INTRODUCTION

THE interaction of radiation with a thermally vibrating crystal lattice is equivalent to the case of radiation scattered from a vibrating molecule. In the case of a molecule, the levels manifest themselves as absorption-emission lines in the infrared spectrum and as lines of modified frequency in the visible spectrum, the frequency shift being of the order of 10^{12} out of 10^{14} cps. The latter phenomenon is known as the Raman effect and is of interest here by way of giving a unified picture.

It is possible to study the lattice dynamics of a crystal from the standpoint of the Raman effect. The crystal may be thought of as a giant molecule, the vibrational levels comprising the vast vibration spectrum of the lattice. Experimental and theoretical work has been carried out along this line, notably by Krishnan,[1] Bhagavantam,[2] Placzek,[3] Born,[4] and Smith.[5] However, the use of visible light is generally not permitted since most crystals are opaque to optical frequencies. Furthermore, even for transparent crystals, the interpretation of the experimental data is rather difficult.

One may study crystal lattice dynamics more conveniently with x-rays. In this case a Raman shift does indeed still occur but it is generally below the level of observation, being about 10^{12} out of 10^{18} cps. Fortunately, it is unnecessary to detect this shift in the case of x-ray investigations. Born[4] has shown that the general mechanical treatment of Placzek reduces to the relatively simple and direct interpretation of Laval[6] and James.[7] Their formulation quantitatively relates the diffuse scattering of x-rays to the frequency and wavelength of traveling elastic waves in the crystal. The thermal motion of the lattice is described by a linear superposition of these waves. By measuring the diffuse intensity along directions in reciprocal space of high symmetry, such as the 100, 110, and 111 in the case of cubic crystals, it is a simple matter to obtain dispersion curves of frequency and velocity *vs* wave vector for waves propagating along these axes. It is

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* Assisted at different times by the Armco Foundation Fellowship and the National Science Foundation.

[1] K. S. Krishnan, Proc. Indian. Acad. Sci. **19**, 216 (1944).

[2] S. Bhagavantam, Proc. Indian. Acad. Sci. **11**, 62 (1940).

[3] G. Placzek, *Handbuch Der Radiologie* (Verlag Julius Springer, Berlin, 1934), Vol. 6, Part 2, p. 205.

[4] M. Born, Repts. Progr. Phys. **9**, 356 (1942–2).

[5] H. M. J. Smith, Trans. Roy. Soc. (London) **A241**, 105 (1948).

[6] J. Laval, Bull. soc. franc. mineral. **64**, 1 (1941).

[7] R. W. James, *The Optical Principles of the Diffraction of X-Rays* (G. Bell and Sons, London, 1948), Chap. V.

usually not possible to obtain directly dispersion curves for waves of arbitrary direction because such waves do not possess a pure longitudinal and transverse vibrational character. A number of investigators[8–11] have employed the Laval-James relation to obtain dispersion curves for waves propagating along the symmetry axes of a crystal, from which approximate vibrational frequency spectra and specific heats were calculated.

It is possible to extend the meaning of the Laval-James analysis by relating the dispersion curves to the Born theory of lattice dynamics. This approach allows one to calculate a number of interatomic tensor force constants which are the fundamental quantities governing the vibrational behavior of the lattice. Curien[10] has by this method obtained a set of force constants for α iron (b.c.c.) and Joynson[12] has by a similar method obtained force constants for the hexagonal lattice of zinc.[13] Having experimentally obtained the values of the force constants, one may then obtain a complete frequency spectrum by solving a secular determinant. The secular equation relates frequency to wave vector, and must be solved for a large number of wave vectors distributed throughout an appropriate section of the first Brillouin zone of reciprocal space. From the frequency spectrum, the partition function and specific heat may be calculated. Also, a relation between the elastic constants and the atomic constants may be obtained by considering the long wave limit of the secular determinant. These topics are discussed briefly in the following section. For a more detailed account, the reader should consult the work of Laval[6] and James[7] concerning temperature-diffuse x-ray scattering and the work of Born,[4] Born and Begbie,[14] and Smith[5] concerning lattice dynamics.

II. SECULAR EQUATION AND DIFFUSE X-RAY SCATTERING

Symmetry considerations show that, for a monatomic face-centered cubic lattice, a total of 9 atomic force constants are required to describe general interactions between an origin atom and all neighbor groups out to and including the third. The secular equation for this case is the 3×3 determinant represented by

$$|D(q)-\omega^2 I|=0, \tag{1}$$

composed of the elements

$$D_{ii}(q)=\frac{4}{m}\{\alpha_1''-\alpha_1' C_{jk}-\beta_1'(C_{ij}+C_{ki})+S_i^2(\alpha_2+4\alpha_3 C_{jk})+S_j^2(\beta_2+4\beta_3 C_{ki})+S_k^2(\beta_2+4\beta_3 C_{ij})\},$$

$$D_{ij}(q)=\frac{4}{m}\{S_i S_j \gamma_1'-4\gamma_3 S_k^2+4\epsilon_3(C_{ki}+C_{jk})\},$$

$$\alpha_1'=\alpha_1+2\alpha_3,\qquad \beta_1'=\beta_1+2\beta_3,$$
$$\alpha_1''=\alpha_1'+2\beta_1',\quad \gamma_1'=\gamma_1+2\gamma_3,$$
$$C_{ij}=\cos(2\pi a q_i)\cos(2\pi a q_j),\quad S_i=\sin(2\pi a q_i).$$

ω is the angular frequency of a traveling elastic wave with wave vector $\mathbf{q}=\mathbf{i}q_1+\mathbf{j}q_2+\mathbf{k}q_3$, $|\mathbf{q}|=1/\lambda$, where λ is the wavelength, I is the identity matrix, and $2a$ is the lattice constant. The additional elements of $D(q)$ are obtained by cyclic permutation of the indices i, j, k. The atomic force constants α_1, β_1, and γ_1 describe interactions between an origin atom and its first neighbor group. Similar meaning applies to the other constants, the subscripts denoting the particular neighbor group. The atomic force constants are clearly defined by Cribier.[15] These constants are proportional to the second derivatives in the expansion of the total potential energy. Higher order terms are neglected here but may be treated by perturbation theory. For the special case of central forces, $\alpha_1=\beta_2=0$, $\beta_1=\gamma_1$, and $\epsilon_3=2\gamma_3=2\beta_3=\frac{1}{2}\alpha_3$.

A comparison of the long-wave limit of Eq. (1) with the elastic matrix for a cubic crystal yields the following relations between elastic and atomic force constants:

$$\begin{aligned} ac_{11}&=2\beta_1+2\alpha_2+8\alpha_3+4\beta_3,\\ ac_{44}&=\alpha_1+\beta_1+2\beta_2+2\alpha_3+10\beta_3,\\ a(c_{12}+c_{44})&=2\gamma_1+4\gamma_3+16\epsilon_3. \end{aligned}\tag{2}$$

The elastic constants of Eqs. (2) are understood to be those obtainable from the dynamic (ultrasonic pulse) method.

For a monatomic cubic crystal, connection between the atomic constants of Eq. (1) and the x-ray data is achieved through the relation [Eq. (3)] of Laval and James. Equation (3) gives the first order diffuse scattering, in electron units per atom, in terms of the elastic waves of thermal vibration.

$$I_1=\frac{1}{m}[f^2e^{-2M}]\left|\frac{S}{\Lambda}\right|^2\sum_{j=1}^{3}\frac{E_{qj}}{\nu_{qj}^2}\cos^2(S,f)\cos^2(S,j), \tag{3}$$

$$E_{qj}=\left[\frac{1}{\exp(h\nu_{qj}/kT)-1}+\frac{1}{2}\right]h\nu_{qj}. \tag{4}$$

The quantity $[f^2e^{-2M}]$ is the square of the atomic scattering factor modified by the debye factor e^{-2M} and is obtainable from a separate experiment. For copper,

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[8] Ph. Olmer, Acta Cryst. **1**, 57 (1948); Bull soc. franc. mineral. **71**, 144 (1948).

[9] H. Cole and B. E. Warren, J. Appl. Phys. **23**, 335 (1952).

[10] H. Curien, Acta Cryst. **5**, 392 (1952).

[11] H. Cole, J. Appl. Phys. **24**, 472 (1953).

[12] R. E. Joynson, Phys. Rev. **94**, 851 (1954).

[13] Joynson employed Born's formulation of x-ray scattering instead of that of Laval and James. The Born formulation relates diffuse scattering directly to the atomic constants and so bypasses the aspect of elastic waves.

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

[15] D. Cribier, Acta Cryst. **6**, 293 (1953).

the values of Brindley[16] were used: m is the atomic mass, and $(\mathbf{S}/\Lambda)$ is the diffraction vector, i.e., the difference in wave vector between the incident and reflected x-ray beam. The sum extends over the three directions of vibration j for a given elastic wave vector q, where q is the vector from the nearest Bragg reflection to the terminus of the diffraction vector $(\mathbf{S}/\Lambda)$. ν_{qj} is the frequency of the elastic wave. (S,j) is the angle between the diffraction vector and direction of vibration. E_{qj} is the quantum energy of an elastic wave, and it approaches kT for high temperatures. The value of E_{qj} can be most conveniently obtained by an iterative procedure: assume $E=kT$ and solve for ν_j by Eq. (3). Substitute ν_j in Eq. (4) and so obtain a new value of E which is to be inserted in Eq. (3) and ν_j solved for again. The cycle is repeated until successive values of ν_j agree. This procedure is generally necessary.

In addition to the first order term [Eq. (3)], the total intensity at points in reciprocal space away from Bragg reflections is composed of Compton scattering and higher order temperature diffuse terms. These contributions must be calculated and subtracted from the total intensity before using Eq. (3) to compute dispersion curves of frequency ν *vs* wave vector q. The Compton scattering was taken from Compton and Allison[17] for copper. The second order diffuse term (scattering from two waves) is given by Eq. (5),

$$I_2=\frac{f^2e^{-2M}v}{2m^2}\left|\frac{\mathbf{S}}{\Lambda}\right|^4\sum_Z\int\int\int\sum_i^3\sum_j^3 \times\frac{E_{\alpha i}\cos^2(S,i)E_{\beta j}\cos^2(S,j)}{{\nu_{\alpha i}}^2{\nu_{\beta j}}^2}dq_1dq_2dq_3, \quad (5)$$

where v is the volume of the primitive cell. The sum over Z refers to the number of zones intersecting an imaginary zone centered on the terminus of $(\mathbf{S}/\Lambda)$. The integration is performed over the regious of overlap between this imaginary zone and neighboring zones. By replacing the zones with spheres of the same volume and assuming an average velocity for all waves in the crystal, the second order term can be simplified and evaluated numerically.

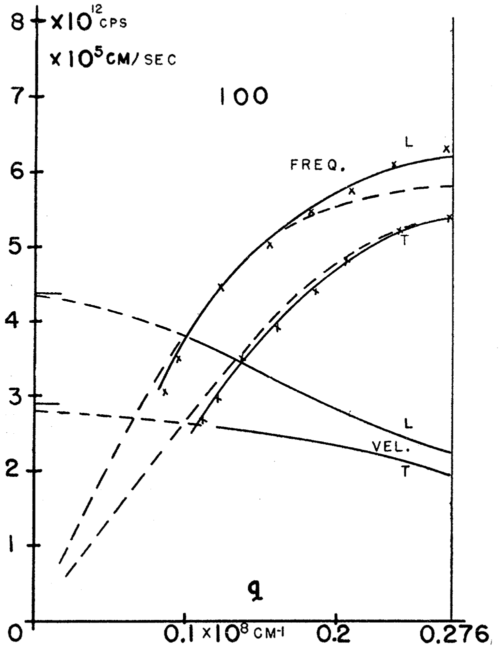

FIG. 1. Frequency and velocity *vs* wave vector for longitudinal and transverse elastic waves propagating in the 100 direction in copper. The solid lines are drawn through the experimental points. The dotted lines are the best fit obtainable and were calculated from the secular equation (1) with the constants of Table I.

In a similar manner the third order contribution can be calculated. For details concerning the method of calculation for higher order terms, the reader should consult reference 8. The maximum contribution of the second and third order terms to the total temperature diffuse scattering is 20 percent and 3 percent respectively. Higher order terms are negligible for copper.

The pure longitudinal and transverse character of waves propagating along the symmetry axes simplifies the first order term [Eq. (3)] for x-ray data taken along these special directions. For example, for $(\mathbf{S}/\Lambda)$ along a symmetry axis, Eq. (3) becomes

$$I_1=\frac{1}{m}[f^2e^{-2M}]\left|\frac{S}{\Lambda}\right|^2\frac{E_{ql}}{{\nu_{ql}}^2},$$

and thereby yields dispersion curves for longitudinal waves. Transverse curves are obtained by measuring intensities along an appropriate line in reciprocal space at right angles to a symmetry axis. In this case $(\mathbf{S}/\Lambda)$ is at some angle ϕ relative to the original longitudinal direction and Eq. (3) becomes

$$I_1=\frac{1}{m}[f^2e^{-2M}]\left|\frac{S}{\Lambda}\right|^2\left\{\frac{E_{ql}\sin^2\phi}{{\nu_{ql}}^2}+\frac{E_{qt}\cos^2\phi}{{\nu_{qt}}^2}\right\}.$$

With the aid of the previously determined longitudinal dispersion curve, one may then obtain the corresponding transverse curve.

These dispersion curves provide the information necessary to determine the inter-atomic force constants through the secular determinant (1). For waves propagating along the symmetry axes, the determinant factors into simple terms. Ideally, by considering a few points along each symmetry axis, such as $q=1/4a$ and $q=1/2a$ for the 100 direction, one may determine all nine atomic constants through a set of simultaneous equations. That is, the frequency obtained from the x-ray data by Eq. (3) is equated to the frequency

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[16] G. W. Brindley, Phil. Mag. 21, 786 (1936).

[17] A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand Company, Inc., New York, 1935).

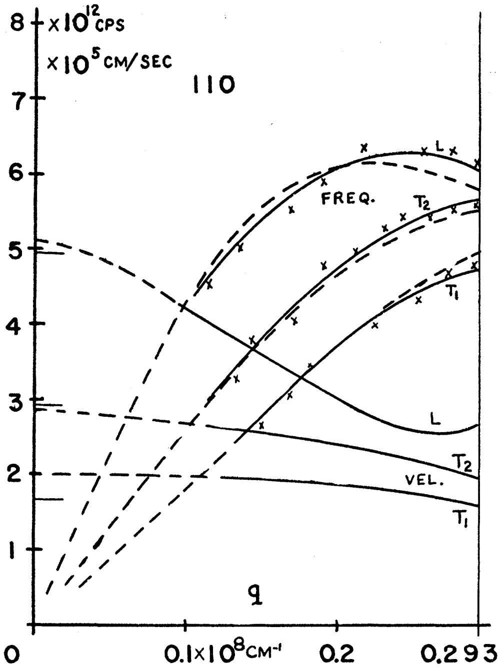

FIG. 2. Frequency and velocity *vs* wave vector for longitudinal and transverse elastic waves propagating in the 110 direction in copper. The solid lines are drawn through the experimental points. The dotted lines are the best fit obtainable and were calculated from the secular equation (1) with the constants of Table I.

appearing in the secular determinant Eq. (1) for the particular wave vector being considered. Actually it was necessary here to so choose the atomic force constants as to give the best over-all fit with the x-ray dispersion curves because not all the data were self-consistent.

III. EXPERIMENTAL PROCEDURE AND RESULTS

Three copper crystals were prepared from a single crystal of 99.99 percent purity for which we are indebted to Professor B. L. Averbach of the Department of Metallurgy. The three crystals were cut with faces parallel to the 100, 110, and 111 planes respectively. Each face was polished and then etched with ferric chloride. Laue photographs taken at several points on each face revealed sharp crystalline reflections.

All temperature diffuse measurements were made at about 300°K with Cu $K\alpha$ radiation from a full-wave rectified copper target tube operating at 35 kv and 21 ma. The radiation was monochromated by a bent lithium fluoride crystal and then passed through a balanced nickel-iron filter to cancel the half-wavelength component. The beam divergence was limited to $\pm 0.5°$ both vertically and horizontally. The scattered radiation was detected by a Geiger counter and was recorded at each angle setting for 20-minute intervals for both the nickel and iron positions of the balanced filter. The face of each copper crystal was so oriented as to maintain equal angles relative to the incident and diffracted beam in order to keep the absorption correction angularly independent. The air scattering was subtracted from the total recorded counts, the remainder being converted to electron units per atom by comparison with radiation scattered from a block of paraffin at large angles.

Intensity measurements taken along the 100 direction between 200 and 400 provided the longitudinal dispersion curve of Fig. 1 through Eq. (3). This curve together with data recorded along the line 400 to 410 produced the 100 transverse dispersion curve also shown in Fig. 1. In the same manner longitudinal and transverse curves for the 110 direction were obtained from intensity data along 5/4, 5/4, 0 to 11/4, 11/4, 0 (long.), 200 to 11/4, 5/4, 0 (trans. 1), and 400 to 4, 3/4, 3/4 (trans. 2). Similarily, the 111 dispersion curves were obtained from data along 3/2, 3/2, 3/2 to 5/2, 5/2, 5/2 (long.) and 222 to 311 (trans.). These results are shown in Figs. 2 and 3. It is to be understood that the dispersion curves are obtained from the average values of intensity measurements made in equivalent regions of a Brillouin zone. The solid lines are drawn through the experimental points. The dotted lines are the best over-all fit presently obtainable with the experimental curves and are derived from the secular determinant [Eq. (1)] with the choice of force constants given in Table I. Shown in Table II is the comparison with elastic constants through Eqs. (2).

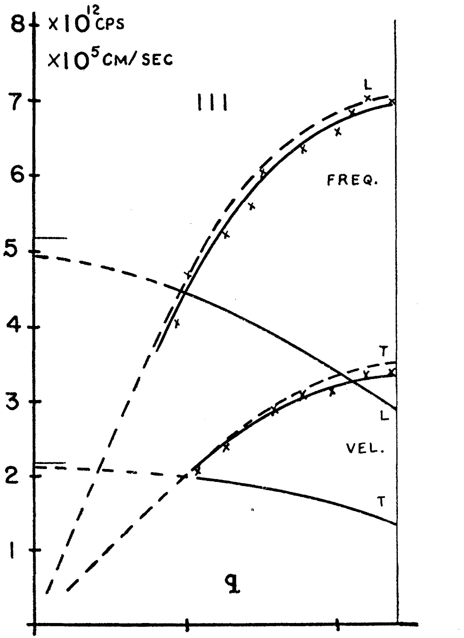

FIG. 3. Frequency and velocity *vs* wave vector for longitudinal and transverse elastic waves propagating in the 111 direction in copper. The solid lines are drawn through the experimental points. The dotted lines are the best fit obtainable and were calculated from the secular equation (1) with the constants of Table I.

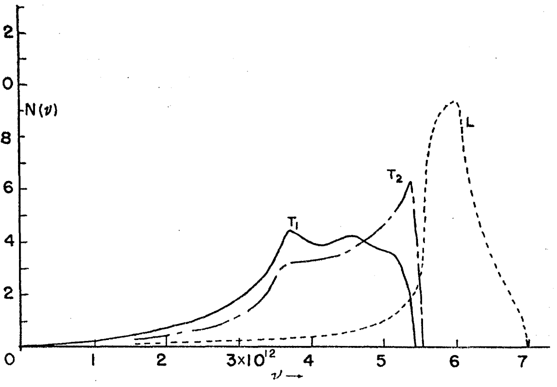

FIG. 4. Decomposition of the vibrational frequency spectrum of copper into "longitudinal" and "transverse" branches for 3417 wave-vector solutions of Eq. (1) employing the general force constants of Table I.

A vibrational spectrum has been calculated from the roots of the secular determinant [Eq. (1)] for 3417 wave vectors distributed uniformly throughout 1/48 of a Brillouin zone.[18] This calculation employed the general atomic force constants listed in Table I and will be referred to here as the general force spectrum. A decomposition of this spectrum into "longitudinal" and "transverse" branches is given in Fig. 4. The composite general force spectrum (solid line) is compared with the central force[19] (broken line) and Debye (dotted line) spectra in Fig. 5. The central force calculation utilized the constants given by Leighton[20] appropriate to copper at room temperature. This approximation is equivalent to the following: $\beta_1=\gamma_1=1.355\times10^4$ dynes/cm, $\alpha_2=-0.0244\times10^4$ dynes/cm and all other constants are zero. Both the general force and central force spectra contain the same number of solutions and were calculated on the M.I.T. Whirlwind I electronic computer.[21] The Debye curve of Fig. 5 was adjusted to have the same area and cut-off frequency as the general force spectrum. This cut-off frequency, ν_m, is 7.01×10^{12} cps and corresponds to a Debye temperature of $\theta=335$°K using the relation $h\nu_m=k\theta$. The cut-off frequency for the central force spectrum is 7.2×10^{12} cps.

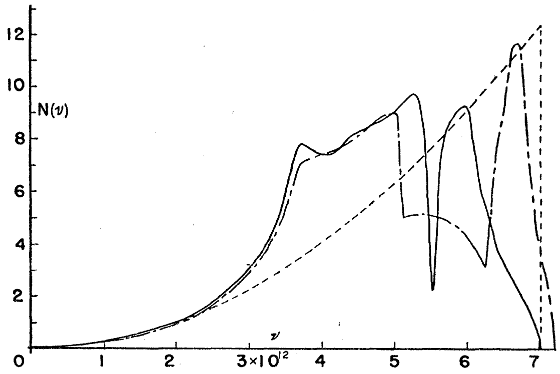

FIG. 5. Comparison of composite general force (solid line), central force (broken line), and Debye (dotted line) spectra for copper. The general force spectrum utilized the force constants of Table I. The central force spectrum utilized the force constants given by Leighton. Both spectra contain 3417 wave vector solutions.

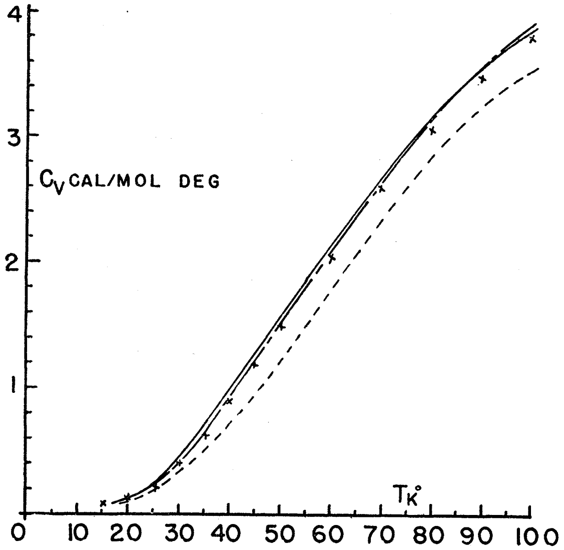

FIG. 6. Calculations of the specific heat, c_v, for copper from the spectra of Fig. 5. The solid, broken, and dotted lines correspond to the general force, central force, and Debye spectra respectively. The crosses are the experimental points of Giauque and Meads.

The specific heat curves of Fig. 6 were calculated by numerical integration from the spectra of Fig. 5 by the relation $c_v=k\int_0^{\nu_m}N(\nu)E(\nu,T)d\nu$, where

$$E(\nu,T)=(h\nu/kT)^2\exp(h\nu/kT)/[\exp(h\nu/kT)-1]^2.$$

The experimental specific heat values were taken from the work of Giauque and Meads.[22] Strictly speaking these specific heat calculations should have employed the low temperature atomic force constants. Such information is not yet available, although Gaffney and Overton[23] have recently experimentally determined that for copper the elastic constants c_{12}, c_{11}, and c_{44} increased by 2.8 percent, 4.8 percent, and 8.6 percent respectively near absolute zero. This suggests similar changes in the atomic constants which would consequently stretch the vibrational spectrum toward a higher cut-off fre-

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[18] The method is outlined in reference 15.

[19] The term central force as applied to lattice dynamics has a very special meaning: i.e., forces between atoms exist only when a component of relative displacement occurs along the line of centers. No forces are exerted for a small displacement perpendicular to the line of centers. A physical central force, such as that produced by a coulomb field, does not satisfy the latter requirement of no force for small perpendicular displacements, as may be readily verified.

[20] R. B. Leighton, Revs. Modern Phys. **20**, 166 (1948).

[21] Availability of Digital Computer Laboratory time for this problem was made possible by the Office of Naval Research.

[22] W. F. Giauque and P. F. Meads, J. Am. Chem. Soc. **63**, 1897 (1941).

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

quency and so reduce slightly the calculated specific heat at low temperatures. However, this calculation was omitted because such changes in the atomic force constants lie within the present degree of experimental uncertainty. For the same reason the more sensitive plot θ *vs* T was omitted.

IV. CONCLUSION

Interatomic force constants for the face-centered cubic lattice of copper have been determined from x-ray measurements at 300°K and are listed in Table I. These constants describe general interaction between an origin atom and its first, second, and third neighbor groups. From these constants a vibrational frequency spectrum (Figs. 4 and 5) and a specific heat curve (Fig. 6) have been calculated. A spectrum for the special case of central forces is compared with that of the general force model in Fig. 5.

Possible errors in the atomic force constants of Table I may be due to omission of anharmonic terms in the potential energy, omission of more distant neighbor effects, and use of a theoretical value for the Compton modified scattering. Of these, the latter may be very important and as such precludes investigation of the others until its behavior is more precisely established. Experimental determination of the Compton scattering is in general rather difficult but has been achieved by Laval in the cases of aluminum and KCl.[24] His measurements do show deviations to an extent which would modify the apparent diffuse scattering by several percent at a zone boundary. This possibility along with the temperature dependence of diffuse scattering are currently being investigated in this laboratory. Until this information has been acquired, it is not possible to set margins of error for the x-ray-determined force constants. The agreement between atomic and elastic constants for c_{11} and c_{12} via Eqs. (2) may thus be somewhat fortuitous at this stage.

TABLE I. Atomic force constants (in dynes/cm) derived from the experimental dispersion curves of Figs. 1, 2, and 3.

$\alpha_1=0.48\times10^4$	$\alpha_3=0.09\times10^4$
$\beta_1=0.87\times10^4$	$\beta_3=-0.022\times10^4$
$\gamma_1=1.25\times10^4$	$\gamma_3=-0.015\times10^4$
$\alpha_2=0.35\times10^4$	$\epsilon_3=0.06\times10^4$
$\beta_2=-0.072\times10^4$	

TABLE II. Comparison of ultrasonic and x-ray values of elastic constants (in dynes/cm^2).

Ultrasonic values[a]	x-ray values
$c_{11}=17.0\times10^{11}$	$c_{11}=17.0\times10^{11}$
$c_{12}=12.3\times10^{11}$	$c_{12}=12.4\times10^{11}$
$c_{44}=\ 7.52\times10^{11}$	$c_{44}=\ 6.45\times10^{11}$

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

It will be noted that the central force model produces a vibrational spectrum in close agreement with that of the general force model over the first 5/7 of the frequency scale. Furthermore, the general force spectrum exhibits no character essentially different from that of the central force model. Thus the specific heats calculated from both models agree well with one another over the temperature range considered. They also agree quite well with the observed specific heat of copper, although it should be added that the choice of a lower characteristic temperature θ will produce a Debye specific heat which is also close to the observed values in this temperature range.

In connection with the x-ray dispersion curves, the central force model is not so consistant. While this model is in fair accord with most of the curves of Figs. 1, 2, and 3, there are discrepancies of over 20 percent for the 100 longitudinal and 110 (trans. 2) cases. Such discrepancies require consideration of a more general type of force between atoms when dealing with lattice vibrations in copper. This statement disagrees with the theoretical results of Fuchs.[25]

It is felt by this author that the future value of temperature diffuse scattering experiments lies mainly in the determination of interatomic forces in solids. Diffraction experiments, including those with electrons and neutrons, are the only direct means presently available for such determinations. Through the study of interatomic forces, it may be possible to acquire supplementary information about the electronic configuration in some solids, particularly metals, the character of which is necessarily reflected in the tensor force constants of Eq. (1). This topic is in fact being studied by a member of the Solid State and Molecular Theory Group at M.I.T. for copper.

The author is indebted to B. E. Warren for suggesting this problem, and for his continued interest and helpful advice on many occasions. He also wishes to thank F. J. Corbató for help in machine computational techniques, and R. E. Joynson and H. Cole for valuable discussion.

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[24] J. Laval, Bull. soc. franc. mineral. **62**, 137 (1939).

[25] K. Fuchs, Proc. Roy. Soc. (London) **A153**, 622 (1936).