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Effect of Thermal Vibrations on Diffraction from Perfect Crystals. I. The Case of Anomalous Transmission

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The temperature behavior of anomalously diffracted x rays in thick crystals ($\mu_0 t = 20$) of germanium has been experimentally determined. The behavior is consistent with a Debye-Waller factor of $\exp(-1.32M)$ which, from the present state of the theory is unexpected. Theory suggests e^{-M}. The possibility of explaining this behavior in terms of a thermally vibrating standing wave field is presented. The absolute value of the imaginary part of the scattering factor for a nonvibrating atom has been experimentally determined for several reflections. The experiment indicates that this quantity is sensibly independent of angle which is is disagreement with a classical treatment of anomalous dispersion. The possibility of explaining these results by a more refined calculation is discussed.

INTRODUCTION

RECENTLY, much interest has been centered on diffraction from perfect crystals, in particular, on the wave fields that exist within the lattice and the phenomenon of so-called anomalous transmission.[1] One facet of diffraction from perfect crystals which has scarcely been treated experimentally or theoretically is the effect of thermal motion. We have undertaken an experimental study of thermal effects in both the Bragg (reflection from a face) and Laue (transmission through a slab) cases of diffraction. We have reported briefly[2] on the former experiments. In this paper, we present some unexpected experimental results on the effective Debye-Waller factor for anomalous transmission and some contradictory data on the effective size of an absorbing atom in a standing wave field.

NOMENCLATURE

t = thickness of crystal in direction of incident beam.
μ_0 = linear absorption coefficient.
$\bar{\mu}_a$ = atomic absorption coefficient $= \mu_0/N'$, where N' is the number of atoms per unit volume.
$\bar{\mu}_{aj}$ = average atomic absorption coefficient of the jth electron in the wave field.
I_D, I_T = intensity of the diffracted and transmitted beams.
R_D, R_T = integrated intensity of the diffracted and transmitted beams on an angle scale.
N = number of unit cells per unit volume.
F, F_0 = structure factor of unit cell at temperature T and at rest, respectively.
ϵ, ϵ_0 = K times the ratio of the imaginary part of F at (hkl) to (000) of the unit cell, at temperature T and at rest, respectively.
K = polarization factor equal to unity or $\cos 2\theta$ for electric vector perpendicular or parallel to the plane of incidence.
e^2/mc^2 = classical electron radius.
$y = (\theta_{\text{Bragg}} - \theta)\pi(\sin 2\theta)/K(e^2/mc^2)N\lambda^2 F$.
$M = 8\pi^2\langle u^2\rangle \sin^2\theta/(3\lambda^2)$
$\langle u^2\rangle$ = mean square vibrational amplitude.

THEORY

The intensity of the transmitted (I_T) and the diffracted (I_D) beams in symmetrical anomalous transmission is given as [Hirsch,[3] Eqs. (11) and (12)],

$$R_D = \frac{I_D}{I_0} = \frac{1}{2}\frac{\exp(-\mu_0 t)}{(1+y^2)} \cosh\left(\frac{\mu_0 t\epsilon}{(1+y^2)^{\frac{1}{2}}}\right), \tag{1}$$

$$R_T = \frac{I_T}{I_0} = \frac{1}{2}\frac{\exp(-\mu_0 t)}{(1+y^2)} \cosh\left(\frac{\mu_0 t\epsilon}{(1+y^2)^{\frac{1}{2}}} \pm X\right), \tag{2}$$

where $\cosh X = 1 + 2y^2$ and X has the same sign as y.[4] The integrated intensity on an angle scale is

$$R_D = \frac{N\lambda^2(e^2/mc^2)Fe^{-\mu_0 t}\cosh\mu_0 t\epsilon}{\pi \sin 2\theta} \times \int_0^{+\infty} \frac{\cosh[\mu_0 t\epsilon/(1+y^2)^{\frac{1}{2}}]}{(1+y^2)\cosh(\mu_0 t\epsilon)} dy, \tag{3}$$

and the expression for R_T is the same except for the X term in the cosine function of the integral.

For convenience we abbreviate the integral as $\int_D$ and $\int_T$ for the diffracted and transmitted beams, respectively. Expressed as in Eq. (3), the $\int_D$ and $\int_T$ are slowly varying functions of the parameter $\mu_0 t\epsilon$. The two integrals have been evaluated on an IBM 7090 computer for $\mu_0 t\epsilon = 0$ to 30. The results are given in the Appendix.

The main interest in this paper is the temperature behavior of Eq. (3). The two quantities F and ϵ are, in general, temperature dependent. Parthasarthy[5] has

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[1] A review of recent work in this field has been given by G. Borrmann in *Trends in Atomic Physics*, edited by O. R. Frisch, F. A. Paneth, F. Laves, and P. Rosabud (Interscience Publishers, Inc., New York, 1959) and by A. Authier, Bull. soc. franc. minéral. et crist. **LXXXIV**, 51 (1961).

[2] B. W. Batterman, Bull. Am. Phys. Soc. **6**, 109 (1961).

[3] P. B. Hirsch, Acta. Cryst. **5**, 176 (1952).

[4] These equations hold for the case of an incident beam plane polarized with the electric vector perpendicular to the plane of incidence. The diffracted beam for the other polarization is not present in this particular experiment.

[5] R. Parthasarthy, Acta. Cryst. **13**, 802 (1960).

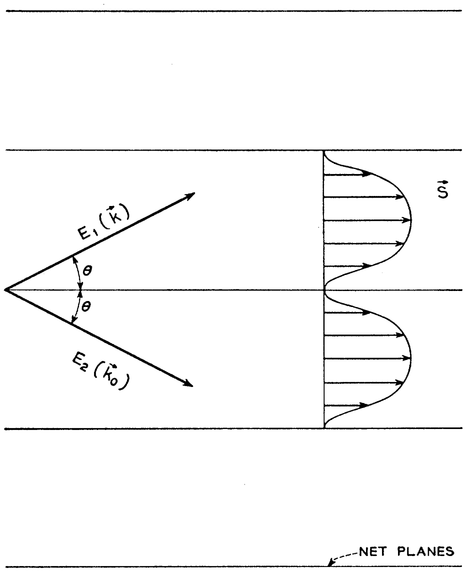

FIG. 1. The wave field of minimal absorption is composed of E_1 and E_2 with wave vectors $\mathbf{k}$ and $\mathbf{k}_0$. The energy flow $\mathbf{S}$ is parallel to, and zero at the net planes.

shown that in certain cases the temperature behavior of F is F_0e^{-M}, where $\exp(-M)$ is the Debye-Waller factor for amplitudes. The temperature dependence of ϵ has not been rigorously treated theoretically. To give a physical picture of the significance of ϵ, we rewrite Eq. (3) in closed form in the limit[6] of $\mu_0t\epsilon$ large:

$$R_D=\frac{N\lambda^2(e^2/mc^2)F_0e^{-M}}{\pi\sin2\theta}\left(\frac{\pi}{8\mu_0t\epsilon}\right)^{\frac{1}{2}}\exp[-\mu_0t(1-\epsilon)]. \quad (4)$$

From the exponential factor in Eq. (4), it can be seen that ϵ in effect determines the anomalously low absorption coefficient, through the factor $(1-\epsilon)$. Thus,

$$\mu_{\text{eff}}=\mu_0(1-\epsilon). \quad (5)$$

If the crystal is thick enough, it has been shown theoretically[3,7–9] and experimentally[10,11] that, in symmetric transmission, the waves existing in the crystal far from the point of entrance can be represented as a standing wave with nodes at the lattice planes and with energy flowing parallel to the planes. This is shown schematically in Fig. 1. The reason for the anomalously high transmission is, therefore, that the absorbing atoms in the lattice planes see a reduced electric field intensity and absorb considerably fewer x rays than when the nodal planes occupy random positions in the lattice.

For the reflections studied in this work, (220) and (400), all the atoms in the germanium structure scatter in phase, and ϵ is simply the ratio of the imaginary part of the atomic scattering factor at the (hkl) reflection, $f''(hkl)$, to the value for the (000) reflection, $f''(000)$. The latter term is directly proportional to the atomic absorption coefficient $\bar{\mu}_a$ of the germanium atom.

The angular dependence of the imaginary part of the scattering factor represented by $f''(hkl)$ is not a clearly defined quantity. If we treat the problem semiclassically (Zachariasen,[12] p. 95, and Batterman[13]) $f''(hkl)$ is the sum of the atomic absorption coefficients of each electron, $\bar{\mu}_{aj}$, weighted by the form factor of that electron. This may be expressed as follows:

$$\epsilon=\frac{f''(hkl)}{f''(000)}=\frac{\sum_j\bar{\mu}_{aj}f_j(hkl)}{\bar{\mu}_a}, \quad (6)$$

where $\sum_j\bar{\mu}_{aj}=\bar{\mu}_a$, and $f_j(hkl)$ is the form factor for the jth electron at a given temperature. When treated strictly quantum mechanically, it is not obvious that the angular dependence of $f''(hkl)$ is so simple. This point will be discussed in more detail in a later section. With the particular conditions of this experiment (CuK_α radiation on germanium), $\mu_{aK}=0$, and most of the absorption takes place in the L shell.

Physically, ϵ can have a value no higher than unity. This would be the case when the atom behaved in effect as a point atom with $f_j=1$. Even if the absorbing electrons are close enough to the nucleus to be considered point electrons, the value of ϵ should still be less than unity because of thermal vibrations.

The question to be answered both by theory and experiment is then: How are thermal vibrations to be taken into account in Eq. (6)? The customary approach when considering thermal motion in perfect crystal diffraction is to argue that one can merely replace the stationary structure factor F_0 by F_0e^{-M}. As pointed out above, it is only recently that a rigorous theoretical treatment has been attempted[5] to show that this is valid in the Bragg and Laue cases when no absorption is present, and preliminary experimental evidence[2] to justify this in the Bragg case has only been attempted in the past few years. If one applies this argument to anomalous transmission where absorption is present, one would account for thermal motion by representing ϵ by $\epsilon_0\exp(-M)$, which follows by replacing the $f_j(hkl)$ in Eq. (6) by $f_j(hkl)\exp(-M)$.

We can arrive at this result in a less arbitrary way by invoking an intuitive argument similar to one used by Borrmann[7] to arrive at an expression for the minimal absorption coefficient in anomalous transmission. We present the details of this in the Appendix, and merely

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[6] Equation (4) is accurate to 0.6% for the value of $\mu_0t\epsilon$ used in this work. It should be pointed out that the observed integrated intensity, R_D, is very sensitive to ϵ when the latter is close to unity. For instance, at $\mu_0t=20$ and $\epsilon=0.9$ a 1% change in ϵ produces a 20% change in observed intensity.

[7] G. Borrmann, Z. Krist. **106**, 109 (1954).

[8] M. von Laue, Acta. Cryst. **5**, 619 (1952).

[9] W. H. Zachariasen, Proc. Natl. Acad. Sci. U. S. **38**, 378 (1952).

[10] G. Borrmann, Z. Physik **127**, 297 (1950).

[11] H. N. Campbell, Acta. Cryst. **4**, 180 (1951).

[12] W. H. Zachariasen, *Theory of X-Ray Diffraction in Crystals* (John Wiley & Sons, Inc., New York, 1945).

[13] B. W. Batterman, J. Appl. Phys. **32**, 998 (1961).

state at this point that it gives an $\exp(-M)$ dependence for ϵ.

EXPERIMENTAL

It is the purpose in this experiment to investigate anomalous transmission in thick highly perfect single crystals at elevated temperatures. Since anomalous transmission exists because of a critical match between a standing wave and an extended path of perfect periodicity in the lattice, it is essential that no lattice strain be introduced by mechanical or thermal means. The furnace design has to be such that temperature gradients are kept to a minimum. A schematic view of the furnace is given in Fig. 2. The beryllium windows, which are also a radiation shield, are kept in the vicinity of crystal temperature. The Mylar windows are vacuum tight. For high-temperature work in vacuum or in an inert atmosphere the windows have to be air cooled. The part holding the crystal attaches to an adjustable cylinder so that adjustments of several degrees for the crystal and the entire furnace are possible. The furnace has been operated continuously up to 850°C. Crystal temperature was measured by several thin-wire Chromel-Alumel thermocouples placed near or touching the sides of the specimen. Because of the good thermally conducting helium atmosphere, no difficulty was experienced in measuring the crystal temperature since it was within a fraction of a degree of the surrounding helium. The temperature measurements were made with the crystal in an atmosphere of pure helium obtained by passing the gas through a Linde B molecular sieve[14] kept at liquid-nitrogen temperature.

The crystals were cut from a pulled germanium single crystal containing approximately 4×10^{15} indium atoms per cc and less than 5 dislocations etch pit counts per square centimeter. The crystals were carefully lapped to within 50 μ of the desired thickness and slowly etched in a 1:20 volume parts $HF\text{-}HNO_3$ solution to final size. The amount etched off was several times the depth of the surface abrasion. The crystals were cut into the shape of a T, and held on a quartz rod with a waterglass-powdered quartz cement.

For the (400) measurements, described in a later section, the furnace was used to cool the crystal. This was accomplished by passing dried nitrogen gas through a copper coil immersed in liquid nitrogen and then through the water cooling coils on the furnace jacket. With the help of insulation around the jacket a temperature of -40°C was reached.

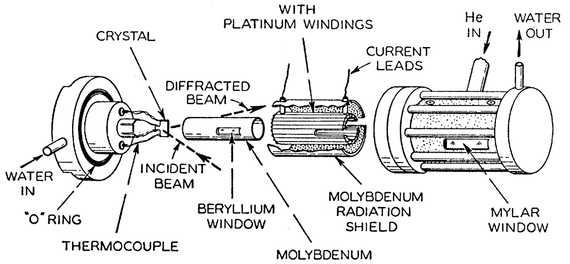

FIG. 2. Schematic diagram of crystal furnace.

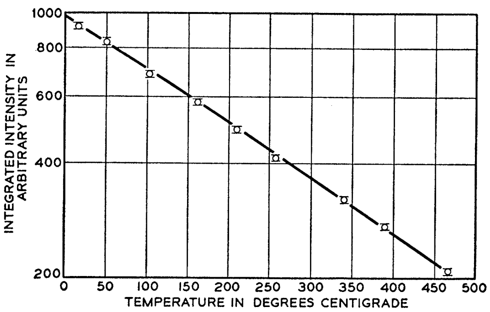

FIG. 3. Log integrated intensity of the anomalously diffracted (220) reflection of germanium vs temperature.

The first crystal of the double crystal spectrometer was a germanium crystal diffracting in the (333) position. Since the Bragg angle is very nearly 45°, the diffracted beam (which is the primary beam for the crystal being studied) is completely plane polarized. The operating conditions of the copper target tube were 30 kv and 15 ma. No difficulty was experienced with short- or long-wavelength harmonics. For an integrated intensity measurement, the crystal was rotated with uniform angular velocity through the α_1 and α_2 copper K doublet well into the background. Separate background counts were taken at fixed points on either side of the peak. The detector consisted of a NaI thallium-doped scintillation counter in conjunction with a pulse height discriminator. The primary beam was monitored by a second counter set to pick up radiation scattered from the first crystal. All counting rates were kept within the linear range of the detecting system.

Because of physical limitations in the furnace we investigated only the anomalously diffracted beam as a function of temperature. At room temperature, both diffracted and transmitted beams were measured.

RESULTS

The measurements for the diffracted (220) and (400) reflections of germanium as a function of temperature are shown in Figs. 3 and 4. Within an experimental error of ±2%, both curves are linear in the logarithm of the integrated intensity. The (220) curve in Fig. 3 is a heating curve, i.e., all data are taken above room temperature. The (400) curve in Fig. 4 contains both heating and cooling data and shows some interesting experimental difficulties which are worth discussing. The points indicated with the circles were the initial set of data taken. The curve is linear below and slightly above room temperature, but decreases more rapidly than linearly as the temperature increases. The curve indicated by the triangles represents data taken under identical conditions, except that the crystal was trans-

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[14] Available from Linde Air Products, Inc., New York, N. Y.

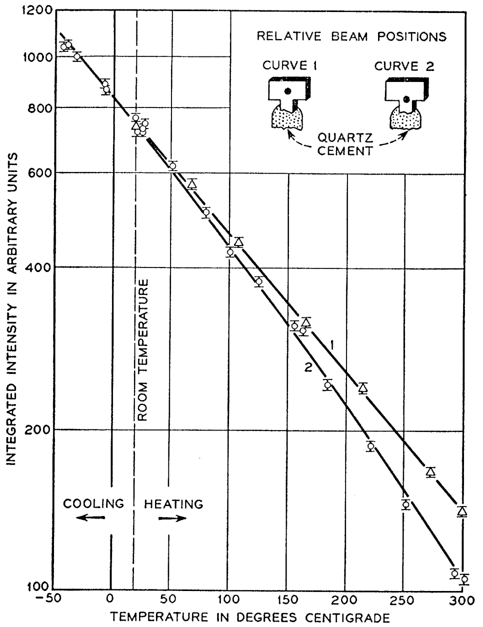

FIG. 4. Log integrated intensity for the (400) diffracted beam vs temperature. The inset shows the relative position of the incident beam and the crystal for the two curves.

lated so that the beam (with a cross section of approximately 0.5×0.2 mm) entered the crystal 1-mm further distant from the quartz mount. (These positions are shown schematically in the figure.) Upon examination of the point of contact between the crystal and the quartz holder it was observed that the quartz cement was not symmetric on either side of the crystal. Thus the most probable explanation of the lower curve in the figure is that mechanical strain produced by a temperature gradient across the specimen near the point of entrance of the beam caused a reduction in the anomalously transmitted beam. The quartz specimen holder is withdrawing heat from the hot region because its lower end is cooled. When the crystal was translated 1 mm, the beam was far enough from the strain point so that the data were not affected. At lower temperatures the two curves converge and agree at room temperature where no gradients can exist.

One critical point to be considered in these measurements is the effect of thermal gradients. One must show strong evidence that the reduction of intensity with increasing temperature is a real diffraction effect for a perfect crystal and is not due to a thermally produced strain in the specimen. Borrmann and Hildebrandt[15] Hildebrandt,[16] and Hunter[17] have shown that strain produced mechanically, or by a thermal gradient, can strongly affect the intensity of both the anomalously transmitted and diffracted beams. An explicit experiment to show if this strain effect exists would be an intensity measurement upon cooling. In a heating experiment both strain and temperature cause a *reduction* of intensity. In cooling, however, the effects are opposed, since the reduction in thermal vibrations should increase the transmitted energy while strain would still decrease it. The cooling experiment was performed for the (400) reflection. The results, as shown in Fig. 4, were a straight line dependence extrapolating very well from the heating curve.

A further check on the effect of a thermal gradient was made as follows: With the furnace removed, a jet of cooled air at 10°C below room temperature was blown only on the exit face of the crystal. The integrated intensity increased, corresponding to the amount the crystal was cooled, (ascertained by a temperature measurement of the crystal) and thus showed no measurable effect of a thermal gradient. These checks give very strong evidence that the observed temperature behavior is a result of changing vibrational amplitudes and is not due to strain effects.

If we now use Eq. (4), together with assumption of an $\exp(-M)$ temperature behavior, it can readily be shown that, neglecting second-order terms, the slope of a plot of $\ln R_D$ vs T is

$$-\frac{d(\ln R_D)}{dT}=\frac{dM}{dT}\left(\tfrac{1}{2}+\mu_0 t\epsilon_0\right). \tag{7}$$

The Debye model relates M and θ by

$$M=\frac{6h^2T}{gk\theta^2}\left(\varphi(x)+\frac{x}{4}\right)\left(\frac{\sin\theta}{\lambda}\right)^2, \tag{8}$$

where g is the mass of the germanium atom and $[\varphi(x)+x/4]$ is the Debye function for amplitudes which is a slowly varying function of temperature. In determining θ from the slopes of Figs. 3 and 4 the Debye functions was evaluated at the average temperature of the experimental run. From the slopes are calculated $\theta_{220}=254$°K and $\theta_{400}=257$°K, which, although they agree internally, are not at all consistent with a room temperature Debye θ from specific heat data in the vicinity of 365°K.

Our initial interpretation of the data was based on a Debye temperature in the vicinity of 360°K, a value consistent with recent heat capacity measurements[18–20] and neutron diffraction[21] results. When the assumption was made that the temperature dependence of ϵ is $\exp(-2M)$, the slopes of Figs. 3 and 4 gave for the Debye temperature $\theta_{220}=354$°K and $\theta_{400}=358$°K, in very good agreement with the specific heat value.

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[15] G. Borrmann and G. Hildebrandt, Z. Naturforsch. **11a**, 585 (1956).

[16] G. Hildebrandt, Z. Krist. **112**, 312 (1959).

[17] L. P. Hunter, J. Appl. Phys. **30**, 874 (1959).

[18] P. J. Flubacker, A. J. Leadbetter, and J. A. Morrison, Phil. Mag. **4**, 273 (1959).

[19] R. W. Hill and D. H. Parkinson, Phil. Mag. **43**, 309 (1952).

[20] I. Estermann and J. R. Weertman, J. Chem. Phys. **20**, 972 (1952).

[21] B. N. Brockhouse and P. K. Iyengar, Phys. Rev. **111**, 747 (1958).

TABLE I. Absolute experimental integrated intensities and corresponding values of ϵ for the (220) and (400) reflections in anomalous transmission.

hkl	$R_D \times 10^6$	$R_T \times 10^6$	ϵ exp(25°C)	ϵ exp(Hunter)	R_T/R_D Exp.	R_T/R_D Theory
220	2.16_2	2.482	0.974	0.964	1.15	1.117
400	0.458_9	0.503_2	0.917	0.921	1.10	1.133

Consequently, it was concluded that the Debye-Waller factor is $\exp(-2M)$, not $\exp(-M)$, in anomalous transmission.

In a subsequent investigation,[22] the mean-square vibrational amplitude of the germanium atom was determined from the temperature dependence of the Bragg reflections of finely powdered germanium. The results gave a mean square amplitude Debye temperature, for germanium of $\theta_M = 291°\text{K}$, differing by about 22% from the specific value $\theta_D = 360°\text{K}$. We have shown that this difference is real and can be explained directly from the frequency distribution of normal vibrational modes of germanium.

To express our results in terms of a Debye-Waller factor, we assume that ϵ is represented by $\epsilon = \epsilon_0 e^{-\alpha M}$, where α is an experimental parameter and M is the amplitude factor appropriate to a Debye temperature of 291°K. From Eq. (4) it follows that the slopes in Figs. 3 and 4 are given by

$$\text{slope} = -(1-\alpha/2)k - \mu_0 t \epsilon_0 \alpha k e^{-\alpha M}, \tag{9}$$

where $k = M/T$. The equation is solved for α with the exponential evaluated at the mean temperature of the run. The solution of Eq. (9) for the two reflections gave $\alpha_{220} = 1.30$ and $\alpha_{400} = 1.33$. Thus, the empirical temperature behavior of ϵ is $\epsilon = \epsilon_0 \exp(-1.32 M_{291°\text{K}})$. It is coincidental that this factor is algebraically equivalent to $\exp(-2M_{355°\text{K}})$.

Before investigating the consequences of the slope data, a description of the measurement of the absolute integrated intensities of the anomalously transmitted and diffracted beams is in order. With the furnace and cover removed, it was possible to measure both beams separately by placing the scintillation counter in either the primary or diffracted beam directions. For an absolute measurement, two independent methods were used to ascertain the primary beam intensity, which was the order of 10^5 cps. The methods are described in the Appendix. The results for the absolute measurements are given in Table I. Using Eq. (4), a value of $\epsilon(hkl)$ can be calculated. These results and the experimental values of Hunter[23] are also given in Table I. The present value of ϵ_{220} is higher than Hunter's, (indicated greater transmission) by 0.9%, while the ϵ_{400} is lower by 0.6%. A significant experimental quantity, independent of the absolute measurement is the ratio of the anomalously transmitted and diffracted beams. These are also given in Table I, together with the theoretical ratio, the latter being sensibly independent of the choice of Debye-Waller factor. The ratios agree with theory to within 3% which is within experimental error.

DISCUSSION

The present experiment has an important bearing on several aspects of both dynamical diffraction theory and published experimental results. The conclusions to be drawn from this work can be separated into two nearly independent portions. One is the temperature behavior of a given reflection, and the other is the absolute value of ϵ for each reflection.

The straightforward conclusion concerning the temperature behavior is that the temperature factor for the anomalously diffracted beam is experimentally shown to be $\exp(-1.32M)$ and not $\exp(-M)$. The conclusion is reached, not from an assumed value for M based on a Debye temperature from specific heat measurements, but is based on an M value experimentally determined from the temperature dependence of the Bragg reflections of a mosaic powder of germanium.

We can reinforce our intuitive ideas concerning the absorption of a vibrating atom in a standing wave field by a quantitative argument. Consider the wave field of Fig. 1 which is the result of two plane waves of equal amplitude traveling in the primary and diffracted beam directions. It is a simple matter to calculate from these plane waves the Poynting vector as a function of position between the planes. Next we place an atom on one of the net planes and let it vibrate with some mean square amplitude $\langle r_n^2 \rangle_{\text{av}}$, where r_n is the component of the amplitude perpendicular to the net planes. If it is now assumed that the probability of photoelectric absorption is proportional to the Poynting vector at the position of the electrons between the planes, we find that the time average of the absorption coefficient has a factor $(1-\epsilon)$ as in Eq. (5) and that $\epsilon = \epsilon_0 \exp\{-8\pi^2[(\sin\theta)/\lambda]^2 \langle r_n^2 \rangle_{\text{av}}\} = \epsilon_0 e^{-M}$, where ϵ_0 is the value for a stationary atom. In order to keep the present argument simpler, the details of the calculation are given in the Appendix. The point to be made is that an intuitive treatment of a vibrating atom in a stationary wave field gives a value for ϵ which is modified by $\exp(-M)$ and not $\exp(-1.32M)$ and this is contrary to experiment. At this point we can only speculate where

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[22] Performed with D. R. Chipman and submitted to this journal.

[23] L. P. Hunter, Koninkl. Ned. Akad. Wetenschap. Proc. **61**, 214 (1958); IBM J. Research Develop. **3**, 106 (1959). Note: Hunter's ϵ values have been corrected for an experimentally determined absorption coefficient of CuK_α radiation in germanium. The method is described in the Appendix.

TABLE II. Comparison of experimental and theoretical values of ϵ.

	ϵ (25°C) exper.		ϵ theory	
hkl	Present work	Hunter[a]	$[\Theta=360°\text{K}, e^{-M}]$	$(\Theta=291°\text{K}, e^{-1.32M})$
220	0.974	0.964	0.939	0.916
400	0.917	0.921	0.884	0.843
422		0.879	0.836	0.778
440		0.828	0.796	0.723

[a] See reference 23.

the error might be. In the treatment just presented we have kept the field stationary and the atom vibrating. This may very well be where the difficulty lies. Since the wave field itself is created by vibrating atoms, it is conceivable that the field is not static with respect to the average net planes, but vibrates with a positional variation comparable to those of the thermally agitated atoms. The experiments of Cole and Brock[24] show that the wave will follow the crystal planes even if the planes are bent, and this implies that the wave field is sensitive to local atomic positions. Thus, from the frame of reference of a single atom, the field may be vibrating in a manner close to that of its neighboring atoms. If this is indeed the case, the field vibrates very nearly in a random phase with respect to the atom in question, and in the calculation, a double averaging must take place; one of a stationary field and a vibrating atom, and the other, a field vibrating with respect to a stationary atom. If the average vibrational amplitude of the field is equal but at random phase with the absorbing atom, the absorptive behavior will now be $\exp(-2M)$, one M from each half of the double average. If, however, as is more likely, the field vibrates with an amplitude which is not exactly equal to or at random phase with that of the atoms, the absorption factor would be somewhere between $\exp(-M)$ and $\exp(-2M)$. The quantitative aspects of this argument are obviously not firmly supported. We merely offer as an *ad hoc* speculation that the $\exp(-1.32M)$ behavior may be explained by the concept of independently vibrating nodal planes of the standing wave field. In any event we conclude that a careful re-examination of dynamical diffraction theory including thermal motion is necessary.

Since the experimental temperature dependence of ϵ is known, one can compare the absolute value of ϵ with predictions of theory. In Table II are the absolute values of ϵ measured at room temperature in this work, and that of Hunter.[23] The independent results for the (220) and (400) are in rather good agreement. The present ϵ_{220} is greater than Hunter's, and this lies in the direction of higher perfection for the crystals in this work. This may be either a result of the errors in the different absolute measurements or actually due to higher crystalline perfection. Hunter found it necessary to apply corrections to ϵ as high as 4%, due presumably to internal strains. Our ϵ_{220} is slightly larger even than Hunter's strain corrected value. The fourth column in Table II gives the theoretical values reported by Batterman[13] using $\exp(-M)$ for the temperature behavior and an ϵ_0 as defined classically in Eq. (6) and calculated from the treatment of anomalous dispersion by Parratt and Hempstead.[25] The values have been changed slightly in that the Debye temperature was changed from 400° to 360°K to conform with specific-heat Θ_D. The agreement must be considered remarkably good[26] especially since an incorrect form for the Debye factor, i.e., $\exp(-M_{360°\text{K}})$ was used in the calculation. Using the experimental factor $\exp(-1.32M_{291°\text{K}})$ and the same ϵ_0 values as before, the values in the last column of Table II were determined. These are in very poor agreement with experiment, and it must be concluded that the accord between theory and experiment in the initial calculation was fortuitous.

An experimental value of ϵ_0 for a stationary atom can be obtained from the room temperature ϵ values and the experimental factor $\exp(-\alpha M)$, since $\epsilon_0=\epsilon\exp(+\alpha M)$. These ϵ_0 values for a stationary atom are given in Table III. It should be noted that they are independent of the choice of the form of the temperature factor and depend only on the observed variation of intensity with temperature. The surprising result here is that the ϵ_0 for all reflections are within experimental error of unity. The semiclassical treatment leading to Eq. (6) gives for ϵ_0

$$\epsilon_0=\left[\textstyle\sum_j \bar{\mu}_{aj} f_j^0(hkl)\right]/\textstyle\sum_j \bar{\mu}_{aj}. \tag{10}$$

If, for simplicity, we assume that all absorption takes place in the L shell (i.e., all $\mu_{aj}=0$ except μ_{aL}), Eq. (10) reduces merely to the form factor of the L electrons. The third column of Table III gives the ϵ_0 of Eq. (10) as computed in reference 13, including the M electron contribution. It can be seen that these values are nowhere near unity. Actually they fall off even faster than the L electron form factor (column 2 of Table III) because of the M electron contribution. On the basis of Eq. (10), all the ϵ_0 could be unity, only if we assume that all absorbing electrons have essentially a point distribution with all $f_j^0(hkl)$ equal to unity. This is surely not the case, since the L form factor alone has dropped to

TABLE III. The value of ϵ_0 for a static atom compared with the form factor, f_L, for the L electrons and the theoretical value when M electrons are included.

hkl	f_L	ϵ_0 (theory)	$\epsilon_0=\epsilon\exp(+1.32M)$
220	0.978	0.962	1.010
400	0.956	0.930	1.012
422	0.938	0.900	1.013
440	0.918	0.872	1.000

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[24] H. Cole and J. Brock, Phys. Rev. **116**, 868 (1959).

[25] L. G. Parratt and C. F. Hempstead, Phys. Rev. **94**, 1593 (1954).

[26] The agreement using $\Theta=400°\text{K}$ is even better than the values in column 4, especially for the higher-order reflections. Using 400°K the agreement between theory and experiment for all reflections is 2%.

0.92 at the (440) reflection while inclusion of the M shell reduces ϵ_0 further to 0.87 (Table III).

A possible explanation for this discrepancy lies in the classical assumptions used to derive Eq. (10). The dynamical diffraction theory defines ϵ only as the ratio of the imaginary part of the scattering factor at the *hkl* reflection to that for the (000) forward beam, but it does not commit itself as to how the quantity $f''(hkl)$ is to be calculated. In the classical treatment used by Zachariasen[12] and this author,[13] it is assumed that the total complex scattering amplitude, D_j, from any portion ρdv of the cloud of electron (j) is $D_j\rho_j dv$. Thus, when one integrates over the entire electron cloud, taking path length differences into account, the total amplitude is merely D_j times the usual form factor and this gives rise to the $f_j(hkl)$ appearing in Eqs. (6) and (10).

An exact solution to the scattering problem is of necessity a wave mechanical one.[27] The problem was first treated by Waller[28] and calculations were initially carried out by Hönl[29] for K electrons, and further extended by Eisenlohr and Müller,[30] and Parratt and Hempstead[25] to L and M shells. The Waller scattering formula shows that the total scattering amplitude from an atom involves two parts. The first part represents scattering for wavelengths far from a characteristic frequency giving $f_0 = \int \psi_j{}^* e^{i\varphi} \psi_j dv$, which is the usual real electron form factor. The second term, which gives the anomalous dispersion, involves matrix elements of the electron of the type $\int \psi_{j'}{}^* e^{i\varphi} \,\mathrm{grad}\, \psi_j dv$, where $\psi_{j'}$ and ψ_j represent the electron wave functions in an initial and some excited state. Thus, it is not obvious that the dispersion terms should have the usual form factor dependence f_0. To date, no calculation has been published which gives the wave mechanical angular dependence of the imaginary part of the scattering factor. Most diffraction experiments measure the total amplitude $|f| = |f_0 + f' + if''|$ for which $f''(hkl)$ is a small correction. Consequently, it has not been necessary to make a detailed calculation of $f''(hkl)$. In anomalous transmission, however, one measures in effect *only* the imaginary part $f''(hkl)$, and thus it is necessary to have a more exact calculation than has heretofore been attempted.

The experimental results of this work imply that the wave mechanical treatment should give almost no angular dependence to the imaginary part of the scattering factor for germanium and copper K_α radiation. Equations (6) and (10) predict that ϵ will depend on the x-ray wavelength because the factors $\bar{\mu}_{aj}$ depend on λ/λ_j. For instance, the $\epsilon(hkl)$ for molybdenum radiation should be closer to unity than for copper radiation because most of the absorption would now take place in the K shell for which f_K is very nearly unity for the reflections considered. We have measured the anomalously diffracted beam with monochromatic MoK_α radiation with the same (400) crystal as before and obtained from an absolute measurement at room temperature, $\epsilon(400)[25°\mathrm{C}] = 0.915$. This is almost identical with the value of 0.917 obtained for copper radiation and gives added support to the contention that there is little, or no angular dependence to the imaginary part of the scattering factor. In fact, the $(\sin\theta)/\lambda$ dependence of ϵ is, within experimental error, due entirely to thermal vibrations and independent of the distribution of absorbing electrons.

A word about crystalline perfection is in order. It is difficult to see how crystalline imperfection could explain this peculiar result. If the crystal were not ideally perfect, the measured ϵ values would be too low. Since the maximum value of ϵ is unity, any correction for imperfections would make the experimental ϵ greater than unity, which would be physically unreasonable.

CONCLUSIONS

It can be concluded from these experimental results that the Debye-Waller factor for anomalous transmission in thick crystals of germanium is $\exp(-1.32M)$, not $\exp(-M)$, if the data are to be consistent with an experimentally determined Debye temperature for amplitudes of 291°K. The dynamical theory of diffraction has not yet been applied rigorously to predict the correct temperature dependence. We offer as a speculation that the observed $\exp(-1.32M)$ behavior results because one must consider the possibility that the standing wave is also vibrating with a thermal amplitude. A careful reexamination of the dynamical theory including thermal effects is necessary.

From an absolute measurement of the anomalously diffracted beam as a function of temperature we have arrived at experimental values for the angular dependence of the imaginary part of the scattering factor, f'', for an atom at rest. The values indicate that f'' is very nearly independent of the angle of scattering in disagreement with a semiclassical treatment of anomalous dispersion. The classical calculation could explain experiment by demanding that the germanium atom behave as a point as far as the distribution of absorbing electrons is concerned. This is surely not the case under the present experimental conditions. It is possible that a quantum mechanical calculation such as first performed by Hönl,[29] but with a detailed evaluation of the angular dependence of f'', would give better agreement with experiment.

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[27] The author is indebted to Dr. S. Tamor of the General Electric Research Laboratory for a very helpful discussion of this problem.

[28] I. Waller, Z. Physik **51**, 213 (1928).

[29] H. Hönl, Ann. Physik **18**, 625 (1933).

[30] H. Eisenlohr and G. L. J. Müller, Z. Physik **136**, 491 (1954).

the crystal preparation, and the programming of the computer calculations by W. J. Romanow are gratefully acknowledged.

APPENDIX

A. Absorptive Behavior of an Atom Vibrating in a Standing Wave Field

If we refer again to Fig. 1, we see that the wave field far from the point of entrance of the beam is a standing wave with nodes at the lattice planes. This limiting internal wave is the result of two waves of equal amplitude traveling in the primary and diffracted beam directions.

We represent the electric field amplitude, Fig. 1, for these waves as $E_1 = E_0 e^{i\omega t} e^{i\mathbf{k}_0 \cdot \mathbf{r}}$ and $E_2 = E_0 e^{i\omega t} e^{i\mathbf{k} \cdot \mathbf{r}}$, where $\mathbf{k}_0$ and $\mathbf{k}$ are the wave vectors for the waves in the primary and diffracted directions respectively, and $\mathbf{r}$ is a position vector in the crystal. Two similar expressions consistent with Maxwell's equations represent the associated magnetic field. It is then a straightforward calculation to show that the Poynting vector, $\mathbf{S}$, has components parallel only to the diffracting planes and depends on position perpendicular to these planes in the following way:

$$|\mathbf{S}| \sim 1 - \cos(\mathbf{k} - \mathbf{k}_0) \cdot \mathbf{r}.$$

The vector $\mathbf{k} - \mathbf{k}_0$ is normal to the diffracting plane and has a magnitude $2\pi/d(hkl)$, where $d(hkl)$ is the spacing between the (hkl) planes. For brevity, we set $b_m = 1/d(hkl)$ and $\mathbf{n}$ as a unit vector normal to the diffracting planes. Using complex notation for the cosine function and the fact that the Poynting vector is proportional to the square of the electric field amplitude, E, we have

$$E^2 \sim 1 - \exp(-2\pi i b_m \mathbf{n} \cdot \mathbf{r}). \qquad (11)$$

We invoke the condition that the probability of photoelectric absorption is proportional to the square of the electric field amplitude to compute the absorption of an electron in the field of Eq. (11).

In Fig. 5, let $\mathbf{r}_0(t)$ be the time dependent position of the atomic nucleus, and $\mathbf{r}$ the vector to the volume dv which contains the fraction $\rho(\mathbf{r}_j)dv$ of electron j. $\mu_{aj}(\mathbf{r})$ is the atomic absorption coefficient of electron j in the wave field at point $(\mathbf{r})$, and $\bar{\mu}_{aj}$ is the average absorption coefficient in the wave field [see Eq. (6)]. We then can write

$$\mu_{aj}(\mathbf{r}) = \bar{\mu}_{aj}[1 - \exp(-2\pi i b_m \mathbf{n} \cdot \mathbf{r})]. \qquad (12)$$

This follows from Eq. (11) and the normalizing condition that the average value of $\mu_{aj}(\mathbf{r})$ in the wave field must equal $\bar{\mu}_{aj}$.

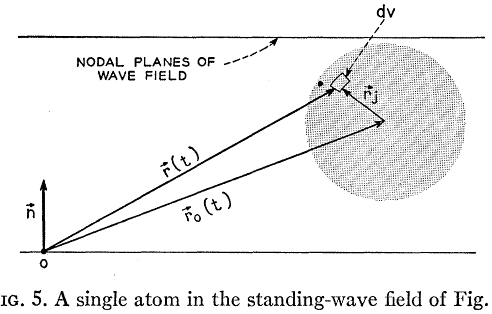

FIG. 5. A single atom in the standing-wave field of Fig. 1.

The value of the atomic absorption coefficient for the entire atom centered at $\mathbf{r}_0(t)$ in the wave field, $\mu_a(\mathbf{r}_0)$, is, using Eq. (12),

$$\begin{aligned}\mu_a(\mathbf{r}_0) &= \sum_j \int_v \mu_{aj}(\mathbf{r})\rho(\mathbf{r}_j)dv \\ &= \bar{\mu}_a - \exp(-2\pi i b_m \mathbf{n} \cdot \mathbf{r}_0) \sum_j \bar{\mu}_{aj} \\ &\qquad \times \int_v \rho(\mathbf{r}_j) \exp(-2\pi i b_m \mathbf{n} \cdot \mathbf{r}_j) dv. \qquad (13)\end{aligned}$$

The last integral represents the stationary form factor of the jth electron f_j^0. Substituting this and factoring out $\bar{\mu}_a$ we get

$$\mu_a[\mathbf{r}_0(t)] = \bar{\mu}_a[1 - \exp(-2\pi i b_m \mathbf{n} \cdot \mathbf{r}_0) \times (\textstyle\sum_j \bar{\mu}_{aj} f_j^0 / \bar{\mu}_a)]. \qquad (14)$$

Comparing Eqs. (6) and (14), we have for the time-dependent atomic absorption coefficient in the wave field

$$\mu_a[\mathbf{r}_0(t)] = \bar{\mu}_a[1 - \exp(-2\pi i b_m \mathbf{n} \cdot \mathbf{r}_0)\epsilon_0], \qquad (15)$$

where ϵ_0 is the static value of ϵ.

For the case where the equilibrium position is in the nodal plane, $\mathbf{r}_0(t)$ represents the displacement due to thermal vibrations. To get the time average of Eq. (15) we need essentially the time average of the exponential on the right, and this is very close in form to that of the Debye-Waller factor $\exp(-2M)$ that appears in diffraction from an ideal mosaic crystal (see James,[31] p. 22).

If we let $2\pi b_m \mathbf{n} \cdot \mathbf{r}_0 = p$, then

$$\langle \exp(ip) \rangle = \exp(i\langle p \rangle) = \exp(-\tfrac{1}{2}\langle p^2 \rangle), \qquad (16)$$

where the angular brackets indicate a time average.

The last step in (16) is a close approximation to that originally derived by Ott[32] and takes into account the fact that the time average of the odd powers in the series expansion of e^{ip} is zero. If we let $\mathbf{r}_n$ be the component of $\mathbf{r}_0(t)$ parallel to $\mathbf{n}$, we have from Eq. (16) and Bragg's law,

$$\exp(-\tfrac{1}{2}\langle p^2 \rangle) = \exp\{-8\pi^2[(\sin\theta)/\lambda]^2 \langle r_n^2 \rangle_{\text{av}}\} = e^{-M},$$

which is merely the square root of the usual Debye-Waller factor. Thus, the dynamical value of ϵ is

$$\epsilon = \epsilon_0 e^{-M}. \qquad (17)$$

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[31] R. W. James, *The Optical Principles of the Diffraction of X-Rays* (G. Bell and Sons, London, 1950), p. 22.

[32] H. Ott, Ann. Physik 23, 109 (1935).

TABLE IV. Tabulation of Eq. (18) as a function of $B=\mu_0 t\epsilon$.

B	$\int_D$	$\int_T$	A
0	1.5375	−1.5375	…
0.5	1.4519	−1.1074	1.7724
1.0	1.2672	−0.2274	1.2533
1.5	1.0854	0.5342	1.0233
2.0	0.9429	0.9996	0.8862
3.0	0.7582	1.2786	0.7236
4.0	0.6489	1.1795	0.6267
5	0.5761	1.0029	0.5605
6	0.5234	0.8447	0.5117
8	0.4506	0.6334	0.4431
10	0.4016	0.5168	0.3963
12	0.3657	0.4458	0.3618
14	0.3381	0.3984	0.3350
16	0.3159	0.3635	0.3133
18	0.2975	0.3364	0.2954
20	0.2821	0.3146	0.2803
22	0.2688	0.2965	0.2672
24	0.2572	0.2813	0.2558
26	0.2470	0.2681	0.2458
28	0.2379	0.2567	0.2368
30	0.2298	0.2466	0.2288

Physically, the reason M appears here, while $2M$ is correct for diffraction from mosaic crystals, is that p in the latter case involves a vector connecting two atoms and the rms length change is twice the value for each of the independent atoms at either end of the vector. In the anomalous absorption case, only the rms amplitude of one atom is involved.

Thus, we see that an intuitive argument predicts a Debye-Waller factor that is equivalent to the expedient of replacing a static atomic scattering factor f_0 by $f_0 e^{-M}$, whereas experiment, on the other hand, does not substantiate this.

B. Numerical Evaluation of Integrated Intensities of Transmitted and Diffracted Beams

The integrals in Eq. (3) for the diffracted beam, R_D, and the corresponding one for R_T, have been evaluated with an IBM 7090 computer as a function of the parameter $\mu_0 t\epsilon = B$.

$$\int_D = \int_0^\infty \frac{\cosh[B/(1+y^2)^{\frac{1}{2}}]}{(1+y^2)\cosh(B)},$$

$$\int_T = \int_0^\infty \left\{\left(\frac{1+2y^2}{1+y^2}\right)\frac{\cosh[B/(1+y^2)^{\frac{1}{2}}]}{\cosh B} - \frac{2}{\cosh B}\right\}dy, \quad (18)$$

$$A = 2\left(\frac{\pi}{8B}\right)^{\frac{1}{2}}.$$

The second term in the integral for the transmitted beam in effect subtracts the background transmission far from the diffracting region. The term approaches zero for thick crystals. For large values of B, $\int_D \rightarrow \int_T \rightarrow A$. The three values of Eq. (18) are given in Table IV.

C. Measurement of Absolute Integrated Intensities

Two independent methods were used to ascertain the primary beam intensity, which was the order of 10^5 cps. The first was an absorption technique described in an earlier publication[33] involving the use of polystyrene as the absorber. The linear absorption coefficient of the material was measured using thin sheets, and a large single piece was accurately machined which reduced the primary beam by approximately a factor of 50 to the linear region of the detector.

In the second method, similar to one described in another work,[34] the (111) integrated reflection of a highly perfect germanium crystal (used as the second crystal in the spectrometer) was measured. Since the first crystal was a germanium (333) reflection and the second crystal now (111), the spectrometer disperses the different wavelength components in the beam diffracted from the first crystal and, hence, at any one setting of the second crystal, the diffracted beam did not exceed the linear region of the detector. From the measured diffracted energy, and an experimental value[35] for the integrated intensity of the (111), $E\omega/I = 0.871 \times 10^{-4}$, the primary beam intensity could be obtained. The two measurements agreed to within 2%.

D. Measurement of the Linear Absorption Coefficient of Germanium for CuK_α Radiation

Single crystals of germanium were carefully lapped to sheets approximately 25 μ thickness and cut into squares 1×1 cm. The transmission coefficient of monochromated CuK_α radiation was measured at approximately 15 points distributed over the 1 cm^2 sheet. From the weight of the crystal, an accurate measurement of the area, and the transmission coefficient, μ_l could be calculated. The result of measurements from three crystals of slightly differing thicknesses is $\mu_l = 352 \pm 2$ cm^{-1}.

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