"Above I"-type damage for copper has been noted as being independent of atomic recoil energy,[1] whereas for aluminum, this quantity decreases with decreasing energy. Another difference between these metals concerns the subthreshold damage which occurs for copper samples[13] but has not been verified for aluminum by the recent experiments of Neely and Bauer.[12] Because of the limited amount of information that is presently available about these effects, their origin is necessarily speculative. It is assumed that these differences in behavior do not depend upon intrinsic properties of a solid, and therefore their interpretation will not conflict with the explanations given in this paper.

To isolate I_C from I_{D+E}, an energy parameter (T_d) is defined. This parameter successfully accounts for the noted energy variation of the I_C and I_{D+E} recovery stages in terms of calculated and experimental curves shown in Fig. 6. To improve the agreement of these calculations, more detailed information must be obtained concerning the functions which describe crystal properties. A second use of the T_d parameter deals with the determination of an energy width ΔT_c. The ratio of ΔT_c of aluminum with respect to that of copper has been calculated from experimental and theoretical work. In terms of the accuracy with which these quantities are presently known, this method of comparing aluminum to copper appears to be quite satisfactory. The present agreement between these values for this ratio certainly justifies further considerations concerning the validity of the T_d parameter.

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Absolute Intensities of X Rays Diffracted in Anomalous Transmission through Nearly Perfect Copper Crystals: A Comparison between Theory and Experiment*

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The absolute integrated intensities diffracted in anomalous transmission through nearly perfect crystals of copper were measured for various wavelengths and reflections by means of a double-crystal spectrometer. Great care was taken to mount and support the crystal in such a way as to minimize the effect of elastic strains. The experimental data are compared with those calculated by using: (1) the formulas of the dynamical theory of diffraction, (2) the semiclassical theory of photoelectric absorption to determine the ratio between the dynamical and the average absorption coefficient, and (3) the experimental value of the average absorption coefficient. The agreement between experiment and theory is satisfactory provided that the Debye temperature of Cu is taken equal to about 300°K. This value is in good agreement with that reported from the dependence of anomalous transmission intensities on temperature, but it is somewhat lower than the Debye temperature (315–317°K) deduced from data obtained by neutron inelastic scattering, Bragg x-ray measurements on powders and single crystals, and calculations from specific-heat data. An analysis is made of the various factors which can influence the experimental or calculated intensities, such as lattice defects, thickness measurements, ratio between dynamical and average absorption coefficients, contribution of the thermal diffuse and Compton scatterings to the absorption coefficient of x rays, and the choice of the Debye temperature.

INTRODUCTION

THERE is extensive literature on the experimental quantitative determination of x-ray intensities diffracted by perfect crystals in the Bragg and in the thin-crystal Laue cases, and the agreement with the values calculated by means of the formulas of the dynamical theory of diffraction is quite satisfactory. Similar measurements on the intensities diffracted in anomalous transmission through thick perfect crystals are scarce. The greater sensitivity of anomalous transmission to small concentrations of lattice defects and to elastic-strain gradients is often an obstacle for obtaining experimental results characteristic of a perfect

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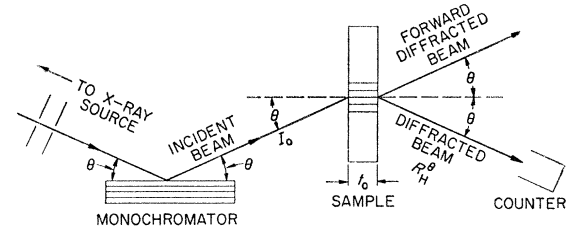

Symetrical Case–Parallel Geometry.

FIG. 1. Diagram of double crystal geometry used for absolute intensity measurements.

crystal. A further impediment, which concerns the precision of the calculated values, comes from the fact that the intensities diffracted through thick crystals are strongly dependent on the difference between the average and dynamical x-ray absorption coefficients, even in the case of low-index reflection. This difference is not known with sufficient precision because of (a) the contributions by the various x-ray scattering phenomena (thermal, photoelectric, and Compton), and (b) the accuracy in the value of the Debye temperature. The average and dynamical absorption coefficients have instead a relatively small influence on the intensities of low-order reflections in the Bragg and thin-crystal Laue cases.

Hildebrandt and Wagenfeld[1] measured x-ray integrated intensities diffracted in anomalous transmission through perfect crystals of Ge with Mo $K\alpha$ and Cu $K\alpha$ radiations, and for several reflections. The value of $\epsilon_H=F''(hkl)/F''(000)$, which they derived from the experimental data, was in good agreement with that calculated by using a semiclassical theory of the photoelectric absorption of x rays. The Debye temperature of Ge, which enters in the Debye-Waller factor $\exp(-M)$ for the imaginary part of the structure factor, was taken equal to the value obtained from experiments on the temperature dependence of diffraction peaks in the Bragg case and from a computation of the frequency spectrum on the basis of neutron inelastic-scattering experiments. Integrated intensities in anomalous transmission for the $\{111\}$ reflections by nearly perfect copper crystals were previously reported by Nicklow, Sherrill, and Young.[2] These authors found that the experimental values of ϵ_{111} were about those which should be expected on the basis of the theory and of the Debye-Waller factor for Cu. The purpose of the present work is to report on absolute measurements of integrated intensities made on the above and other Cu crystals for various reflections and different wavelengths. The experimental data are compared with those calculated by using values of $(\epsilon_0)_H$ for Cu (the subscript 0 refers to a lattice with no thermal vibrations) as calculated by Merlini and Van der Voort.[3] The various factors which can affect the experimental and the calculated intensities are discussed in the light of the available data on the Debye temperature of Cu, and of the possible contributions of Compton and thermal diffuse scatterings to the absorption of x rays.

EXPERIMENTAL PROCEDURE

Absolute integrated intensities were measured by means of a double-crystal spectrometer in the manner described previously.[2] Figure 1 shows the geometrical arrangement for the symmetrical case of anomalous transmission.

In this paper we shall be primarily concerned with only the Borrmann diffracted (or reflected) beam intensities. Although measurements were also made of the Borrmann forward diffracted (or transmitted) beam intensities, these values will not be reported here. The average beam size on the samples was 0.1 cm×0.3 cm. The samples were lamellas 1 cm×1 cm in cross-section acid sawed[4] from 99.999%+copper crystals with a density of dislocation lines $\lesssim 500/\text{cm}^2$ (except for 77-1-3) and were etched in HNO_3 or electropolished to thicknesses t_0 of $0.014\leq t_0<0.22$ cm. Surface preparation was not found to be as critical as that observed for germanium.[5] For samples prepared by etching in HNO_3, small differences in Borrmann intensities were sometimes observed when the entrance and exit surfaces of the crystals were reversed. Subsequent etching nearly always removed these small differences. The sample thickness t_0 was measured nondestructively to a precision of about $\pm 5\,\mu$ with a shadowgraph for crystals of thickness >0.04 cm, or with Ag $K\alpha$ x rays to about 1% for crystals <0.04 cm. Silver, molybdenum, copper, and chromium $K\alpha$ radiations were used, and 111, 200, 220, and 222 symmetrical and asymmetrical reflections were studied.

The principal experimental difficulty in measuring the integrated intensities was in avoiding elastic strain in the lamellas. Most of the crystals had been neutron-irradiated with 10^{17} *nvt* to pin the dislocations and thus avoid accidental plastic deformation. Some of these crystals were soft-soldered to copper handles; others were held in graphite holders by very light pressure contacts. In all cases a number of experiments were carried out to determine whether any elastic strain resulted from the mounting techniques. Borrmann topographs[6] were routinely taken and often showed small elastic strains in the vicinity of the solder junc-

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tions but none in the center of the crystals, where measurements were taken. In the case of crystals mounted in the graphite holders, the pressure contacts were loosened until topographs showed no evidence of strain. In addition, double-crystal measurements were made using both *hkl* and $\bar{h}\bar{k}\bar{l}$ reflections for all crystals; and any elastic strain generally was indicated by a difference in these integrated intensities.[5,7] The pressure contacts were loosened until the integrated intensities for both the *hkl* and $\bar{h}\bar{k}\bar{l}$ reflected beams agreed to within 3%. Also, the ratio of the intensities of the transmitted and reflected beams was compared with the theoretical value.

To measure the power of the incident beam, carefully calibrated absorbers were used for all the crystals. Errors in incident beam intensity are small and, if present, could produce only a small systematic error in integrated intensities.

THEORY

The formulas used for the calculation of the integrated intensities, those given by Kato,[8] and the expressions used to take into account the polarization of the beam reflected by the monochromator were reported in a previous publication.[2] Only the formula of the integrated intensity of the reflected beam R_H for the case of an incident x-ray beam plane polarized is given here with the exact value of h:

$$R_H = \frac{K r_c N \lambda^2 F_H{}^r}{\pi^{1/2}(|b|)^{1/2}\sin 2\theta_B}\left(\frac{1}{8h}\right)^{1/2} e^{-(\mu t - h)} \times\left[1+\frac{1}{8h}+\frac{9}{2}\frac{1}{(8h)^2}+\cdots\right], \quad (1)$$

where r_c is the classical radius of the electron, N is the number of unit cells/cm^3, K is the polarization factor, and $b=\gamma_0/\gamma_H$ is the ratio of the direction cosines of the incident and transmitted beams with respect to the surface normal, respectively. $F_H{}^r$ is the real part of the structure factor for the reflection H, λ is the x-ray wavelength, θ_B is the Bragg angle, μ is the linear absorption coefficient of x rays, $t=t_0/2[1/\gamma_0+1/\gamma_H]$ is the effective thickness of the crystal, and $h=(\mu t_0/2\gamma_0)\times\{(1-b)^2+4bK^2\epsilon^2\}^{1/2}$ and ϵ is the ratio of the imaginary parts of the structure factors for the reflection H and the forward direction. This ratio is equal to that for the imaginary parts of the atomic-scattering factors if all the atoms of the unit cell scatter in phase. In the symmetrical case, $h=\mu t K\epsilon$, and (1) takes the well-known form used elsewhere.[9]

In order to calculate ϵ, the various phenomena which contribute to the absorption of x rays should be taken into consideration. Absorption due to the photoelectric effect only is considered in this section. In fact, phonon excitation and Compton effect are a small contribution to the total absorption coefficient for the wavelengths of interest. However, since the dependence of absorption with the scattering angle is expected to be much greater for Compton scattering and phonon excitation than for photoelectric scattering, one cannot exclude *a priori* a contribution of these scattering phenomena to ϵ, as discussed elsewhere.[10] An evaluation of their influence on the diffracted intensities and on the total x-ray coefficients is examined in the discussion. The theoretical work by Ohtsuki[11] and by Dederichs[12] (in the case of photoelectric absorption) and a number of experimental results[9,13–16] show that the dependence of ϵ on temperature is, to a good approximation, the same as that for the real part of the atomic scattering factor

$$\epsilon=\epsilon_0 e^{-M},$$

where $\epsilon_0=f_{hkl}{}^i/f_0{}^i$ applies to the lattice with the atoms at rest.

Following the procedure of Wagenfeld[17] and of Merlini and Van der Voort,[3] we assume the incident photon to be polarized along the y axis and to have a propagation vector $\mathbf{K}_0$ parallel to the x axis with a wave number K_0. The imaginary part of the atomic scattering factor,[18] which corresponds to transitions of the atomic electron from bound states to continuum states with absorption of the photon, is given at zero scattering angle by[19]

$$f_0{}^i=\frac{\pi\hbar^2}{m}\sum_j\left|\int\psi_{n'}e^{-iK_0x_j}\frac{\partial\psi_j}{\partial y_j}d\tau\right|^2,$$

where the sum $\sum_j$ is extended to all the electrons of the atom, $\psi_{n'}$ is an electron wave function (real) of the continuum (only excitations to continuum states are considered here), and ψ_j is the wave function of the j electron in the atom, $\hbar$ is the rationalized Planck constant, and m is the mass of the electron. The exponential inside the integral is expanded in a Taylor series, and only terms up to $K_0{}^2$ are retained.

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TABLE I. Values of ϵ_0 and $\epsilon_0 \cos 2\theta$ for Ag K_α, Mo K_α, Cu K_α, and Cr K_α radiations, and for a series of reflections.

	Ag $K\alpha$		Mo $K\alpha$		Cu $K\alpha$		Cr $K\alpha$	
hkl	$\epsilon_0^{\perp}$	$\epsilon_0^{\parallel} \cos 2\theta$	$\epsilon_0^{\perp}$	$\epsilon_0^{\parallel} \cos 2\theta$	$\epsilon_0^{\perp}$	$\epsilon_0^{\parallel} \cos 2\theta$	$\epsilon_0^{\perp}$	$\epsilon_0^{\parallel} \cos 2\theta$
111	0.9984	0.9594	0.9983	0.9368	0.9932	0.7065	0.9888	0.3778
200	0.9979	0.9458	0.9977	0.9165	0.9910	0.6165	0.9851	0.1758
220	0.9959	0.8920	0.9954	0.8327	0.9820	0.2404	⋯	⋯
313	0.9943	0.8520	⋯	⋯	⋯	⋯	⋯	⋯
222	0 9938	0.8389	0.9932	0.7513	0.9729	0.0881	⋯	⋯
400	0.9917	0.7857	⋯	⋯	⋯	⋯	⋯	⋯
422	0.9876	0.6812	⋯	⋯	⋯	⋯	⋯	⋯
333 151	0.9861	0.6425	⋯	⋯	⋯	⋯	⋯	⋯

Then

$$f_0{}^i = \sum_j \left[\eta_1{}^{j(0)} + K_0{}^2(\eta_1{}^{j(2)} + \eta_2{}^{j(2)})\right].$$

Here $\eta_1{}^{j(0)}$ is the term corresponding to the electric-dipole approximation. This term, which is usually the only one taken into consideration in the calculation of the photoelectric-effect cross sections, is by far the greatest one. Its expression is

$$\eta_1{}^{j(0)} = \frac{\pi h^2}{m}\left(\int \psi_{n'} \frac{\partial \psi_j}{\partial y_j} d\tau\right)^2.$$

Here $\eta_1{}^{j(2)}$ is the second-order dipole term:

$$\eta_1{}^{j(2)} = -\frac{\pi h^2}{m}\left(\int \psi_{n'} \frac{\partial \psi_j}{\partial y_j} d\tau\right)\left(\int \psi_{n'} x_j{}^2 \frac{\partial \psi_j}{\partial y_j} d\tau\right);$$

and $\eta_2{}^{j(2)}$ is the first quadrupole term:

$$\eta_2{}^{j(2)} = \frac{\pi h^2}{m}\left(\int \psi_{n'} x_j \frac{\partial \psi_j}{\partial y_j} d\tau\right)^2.$$

The expressions for the electric-dipole terms, second-order dipole terms, and the first quadrupole terms, obtained by taking the hydrogenic wave function for the continuum states $\psi_{n'}$ and for the bound states ψ_j of electrons in K, L, and M shells, have been published by Wagenfeld.[17]

In the present work the $\eta_1{}^{j(0)}$ were calculated for copper for the electrons of the K, L, and M shells, the $\eta_1{}^{j(2)}$ and $\eta_2{}^{j(2)}$ for the electrons of only the K and L shells. The calculated values of the linear absorption coefficient for four characteristic wavelengths are given in Table II and are discussed below. From the dependence of the first quadrupole term on the scattering angle,[20] the expression of $\epsilon_0{}^{\perp}$ (relative to the component of the radiation with perpendicular polarization) is obtained;

$$\epsilon_0{}^{\perp} = 1 - \frac{8\pi^2 \sum_j \eta_2{}^{j(2)}}{\left[\eta_1{}^{j(0)} + K_0{}^2(\eta_1{}^{j(2)} + \eta_2{}^{j(2)})\right]}\left(\frac{\sin\theta}{\lambda}\right)^2.$$

A similar expression, but with a different dependence on the scattering angle is found for $\epsilon_0{}^{\parallel}$ (relative to the component of the radiation with parallel polarization). The values of $\epsilon_0{}^{\perp}$ and $\epsilon_0{}^{\parallel} \cos 2\theta$ ($\epsilon_0{}^{\parallel}$ is of interest here only for low-index reflections by relatively thin crystals) are given in Table I for four characteristic wavelengths and various reflections.

RESULTS AND DISCUSSION

The experimental and calculated values of the linear absorption coefficient μ for the four characteristic wavelengths of interest are given in Table II. The contribution μ_{PE} of the photoelectric effect on the electrons of the K, L, and M shells, which is by far the most important part of the total absorption coefficient, was calculated by using the procedure illustrated in the previous section. The inner screening numbers s calculated by Slater were employed to determine the effective atomic numbers $Z-s$.[21] The slightly different screening constants by Duncanson and Coulson[22] give calculated values of μ_{PE} which coincide with those of Table II within the range of the experimental error. It was found that the electrons of the L and M shells contribute about 10 and 2%, respectively, of the amount due to electrons of the K shells in the case of Ag $K\alpha$ and Mo $K\alpha$ radiations. For Cu $K\alpha$ and Cr $K\alpha$ radiations the electrons of the M shells contribute only about 2.5% of the amount due to electrons of the L shell. The contribution μ_{TDS} of thermal diffuse scattering to the absorption, which increases with temperature, was calculated for $T = 295°$K and for an incident beam of unpolarized radiation by using a theory based on the Einstein model for the vibrating crystal.[10] Since the experimental data for μ_{tot} were obtained by measuring the transmission of monochromatic radiation through polycrystalline samples, the contribution μ_{BS} of the Bragg scattering to absorption was calculated by summing the intensities of the rays diffracted by a volume element of a crystalline powder (with no preferred orientations) over all the possible Debye-Scherrer reflections. The x-ray incident beam was assumed to be unpolarized. The contribution from Compton scattering which is included in μ_{tot} is ≈ 1 cm^{-1} in the case of Ag $K\alpha$, Mo $K\alpha$, and Cu $K\alpha$ radiations and somewhat less for Cr $K\alpha$ radiation.[22]

The agreement between experimental and calculated value is very good in the case of the Ag $K\alpha$ and Mo $K\alpha$ radiations, for which photoelectric absorption is mainly due to excitation of electrons of the K shell. For Cu $K\alpha$ and Cr $K\alpha$ radiations instead, the calculated values range 20–30% lower than the experimental ones.

TABLE II. Average linear absorption coefficients μ_i in cm^{-1} for Ag K_α, Mo K_α, Cu K_α, and Cr K_α radiations. PE refers to photoelectric effect, TDS to thermal diffuse scattering, and BS to Bragg scattering.

	Calculated values				Experimental
λ (Å)	μ_{PE}	μ_{TDS}	μ_{BS}	μ_{tot}	$\mu_{(\mathrm{tot})}$
0.561	225	1.84	2.57	229	224±2
0.710	432	2.12	3.83	438	438±6
1.54	337	2.44	11.56	347	446±6
2.29	1061	2.09	13.96	1071	1364±20

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TABLE III. Experimental and calculated values of integrated intensities of Cu crystals. b ($=1$ in the symmetrical Laue case) is the ratio between the direction cosines of the incident and transmitted beams. t_0 is the thickness of the crystal.

			Integrated intensities×10^8								
			Mo *Kα*			Cu *Kα*			Cr *Kα*		
				Calc. Θ in °K			Calc. Θ in °K			Calc. Θ in °K	
Crystal	b	t_0 (cm)	Expt.	300	315	Expt.	300	315	Expt.	300	315
111 reflection											
UC6–10	1	0.014	403.	424.	433.						
UC6–4	1	.027	187.	217.	226.						
1161	1	.0385	130.	139.	146.	206.	202.	214.	33.5	29.0	35.2
UC6–1	1	0.0648	61.3	61.2	66.9						
1162	1	0.0843	31.4	37.0	41.5	53.5	55.0	62.3			
UC6–3	1	0.1255	14.6	14.7	17.4						
UC6–9	1	0.1330	12.8	12.5	15.1						
1163	1	0.2052	2.54	3.11	4.13	3.54	3.27	4.44			
UC6–8	1	0.2174	2.12	2.48	3.35						
U–4	0.88	0.0542	80.8	79.9	86.5	127.	129.	140.			
U–4	1.13	0.0542	73.4	70.7	76.5						
U–5	0.88	0.0556	74.0	76.5	83.0						
U–5	1.13	0.0556	63.6	67.7	73.4						
200 reflection											
1161	1	0.0385	79.8	83.8	89.9	125.	128.	139.	7.41	8.18	10.7
1162	1	0.0843	18.1	18.0	21.0						
220 reflection											
1161	1	0.0385	19.1	19.2	22.1	30.7	28.4	33.6			
1162	1	0.0843	1.63	1.75	2.38						
U–4	1	0.0542	8.27	8.00	9.71	10.4	9.45	11.9			
222 reflection											
UC6–10	1	0.014	51.8	54.9	59.2						
UC6–4	1	0.027	12.3	15.2	17.6						
1161	1	0.0385	6.07	5.93	7.26	5.02	4.59	6.09			
U–4	0.885	0.0542	1.95	1.61	2.18	0.99	0.80	1.20			

This discrepancy for longer wavelengths could probably be eliminated by using Hartree or Hartree-Fock wave functions in place of the simple hydrogenic wave functions. The hydrogenic approximation, which is satisfactory for the K electrons, fails to give a sufficiently accurate description of the excitations of L and M electrons. Since the energy of the incident x rays is much greater than those of the L-absorption edges of Cu, the photoelectric effect can take place well inside the L shell, in regions where the effective screening constant is appreciably less than the average value for the shell. It is worth mentioning that a decrease of 15% in the screening constant of the L-shell electrons determines an increase of about 10% in the calculated value of the linear absorption coefficient of Cu *Kα* and Cr *Kα* radiations.

The results of the integrated intensity measurements are given in Table III. Each entry represents an average of at least four experimental measurements. In general, the experimental scatter was less than 3% and the range of the experimental error is estimated as ±5%. Also listed are two series of values of integrated intensities calculated by using the experimental data of the total absorption coefficients (Table II), the calculated values of ϵ_0 (Table I) and two Debye temperatures $\Theta=315$ and 300°K. Experimental values of the atomic structure factors[23] were used for the calculations. There is a semiquantitative agreement between calculated and measured intensities, but the experimental data are considerably lower than those calculated with $\Theta=315$°K, a disagreement which is well above the range of the experimental error for thicker crystals and higher-order reflections. In order to explain the origin of this disagreement, the following factors which can affect the experimental or the calculated values of the integrated intensities are discussed below: errors in the measurements of the thickness of the crystal t_0 and of the absorption coefficient μ, elastic strain and lattice imperfections present in the crystals, the calculated values of ϵ_0, neglect of the contributions to the dynamical values of the absorption coefficient by the thermal diffuse and the Compton scatterings, and the choice of the Debye temperature used for the calculations.

The relative error in the determination of the thickness t_0 decreases with increasing thickness and with greater surface planarity of the crystal lamellas. If the thickness were the only source of error, the percentage of the difference between experimental and calculated values would remain about constant with an increase in the thickness of the crystal. This is in contrast with the data reported in Table III. By taking various measurements (hkl and $\bar{h}\bar{k}\bar{l}$ for asymmetrical reflections, different hkl, different λ) on the same lamella, the effect of errors in t_0 were minimized. While errors in t_0 and/or nonplanarity of the lamellas may account for much of the scatter in the experimental

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TABLE IV. Relative and absolute intensities of crystal 77–1–3, thickness 0.035 cm. (μ is the linear absorption coefficient of x rays, and t is the effective thickness of the crystal.)

(a) Relative intensities with Ag K_α radiation.

Reflection	μt	Experimental values	Calculated values Debye temperature 300°K	Calculated values Debye temperature 315°K
Laue case				
$\bar{1}1\bar{1}$	8.6	1	1	1
$\underline{020}$	10.1	0.53	0.50	0.50
$\bar{2}0\bar{2}$	15.9	0.091	0.120	0.130
$\bar{1}3\bar{1}$	8.5	0.104	0.134	0.140
$\underline{131}$	21.7	0.0106	0.0144	0.0165
$\bar{2}2\bar{2}$	8.9	0.084	0.104	0.110
$\underline{040}$	9.4	0.018	0.025	0.028
$\bar{2}4\bar{2}$	8.7	0.011	0.016	0.018
$\bar{3}3\bar{3}$	9.6	0.0058	0.010	0.012
$\bar{1}5\bar{1}$	9.6	0.0054	0.0073	0.0086
Bragg case				
222	···	6.3	4.34	4.27
333	···	1.9	1.38	1.38

(b) Absolute intensities$\times 10^8$ in anomalous transmission with Mo K_α radiation.

Reflection	μt	Experimental values	Calculated values Debye temperature 300°K	Calculated values Debye temperature 315°K
111	15.6	122.	152.	162.
222	16.3	5.30	7.44	8.97

results, they cannot account for the discrepancies with the calculated values, especially in the case of thick crystals. If the measured absorption coefficient were slightly less than the true values, the difference between calculated and experimental intensities would increase linearly (in first approximation) with the thickness of the crystal. In fact, it increases with thickness, but the maximum evaluated error in the experimental determination of μ can, at most, account for a small part of the discrepancies found with thick crystals.

As mentioned above, a number of precautions were taken to avoid elastic strain in the lamellas. It was observed that for small strains the average of hkl and $\bar{h}\bar{k}\bar{l}$ measurements yielded good agreement with the value for the unstrained crystal, the latter being defined as that crystal for which both R_H and R_T values of hkl and $\bar{h}\bar{k}\bar{l}$ reflections were equal. Results by other authors[5,7] on the effects of elastic strains in Ge support these observations.

It was reported previously that the presence of a limited number of dislocation lines and/or vacancy clusters did not appreciably affect the measurements of integrated intensity. Measurements of absolute and relative intensities on crystal 77-1-3 containing about 2×10^3 dislocation lines per cm^2 (a factor of 10 higher than in the other lamellas) are given in Table IV. The agreement between calculated and measured absolute intensities with Mo $K\alpha$ radiation is worse than that obtained for more perfect crystals. It appears that dislocation densities of the order of 10^3 lines/cm^2 can affect the integrated intensities in anomalous transmission. This conclusion is supported by the relative intensities obtained with Ag $K\alpha$ for the (222) and (333) reflections in the Bragg case and for higher-order reflections in anomalous transmission. Defects such as large clusters and dislocations were monitored by topographs of the lamellas, but the irradiation used to harden the crystal (in order to avoid plastic deformation) introduced defects which were not visible by this technique. Information concerning the effect of neutron irradiation on intensities diffracted in anomalous transmission will be published elsewhere. As reported earlier,[2] the integrated intensities of crystals irradiated with 10^{17} *nvt* were slightly less than those of crystals irradiated with 10^{16} *nvt*. In order to check this result, crystal UC63, irradiated with 10^{17} *nvt*, was annealed for 2 h at 500, 700, and 900°C. Topographs and intensity measurements were taken before and after each anneal. The same region of the crystal, the original thickness of which was maintained throughout all the experiments, was investigated each time and plastic deformation was avoided by careful handling. No significant change in intensity was observed after the 500 and 700°C anneal, but a small (+6%) increase of the integrated intensity, barely greater than the scatter of the experimental data, was observed after the 900°C anneal. X-ray topographs showed that all of the as-grown vacancy clusters were removed by the 900°C anneal. Therefore, neither the dislocations nor the defects introduced by neutron irradiation can account for the difference between measured and calculated intensities for $\Theta = 315$°K.

The calculated intensities are very sensitive to the value of $\epsilon = \epsilon_0 e^{-M}$. For the {111} reflection, a change in ϵ of only 0.4% can account for the difference between calculated and measured intensities. A variation in the value of ϵ can come about either through the Debye-Waller factor (by changing the Debye temperature) or through the values of ϵ_0 which could be affected by the approximations made in the evaluation of photoelectric absorption. The method employed to calculate ϵ_0 for copper is the same as that used for germanium; in the latter case a good agreement was reported between theory and experiment.[1] A 15% smaller screening constant for the L-shell electrons of copper (a variation which gives 10% higher photoelectric absorption coefficients for Cu $K\alpha$ and Cr $K\alpha$ radiations, as explained above) does not affect appreciably the values of ϵ_0. In addition, for Mo $K\alpha$ and Ag $K\alpha$ radia-

TABLE V. Dynamical values of the thermal-diffuse-scattering linear absorption coefficients at 295°K in cm^{-1} for a series of reflections and Cu $K\alpha$ and Mo $K\alpha$ radiations.

Reflection indices	Dynamical values of μ_{TDS} Cu $K\alpha$	Dynamical values of μ_{TDS} Mo $K\alpha$
111	3.14	3.00
200	2.93	2.93
220	2.16	2.64
222	1.46	2.40

tions the approximations made in the evaluation of the photoelectric quantities ϵ_0 and μ are quite satisfactory. Hydrogenic wave functions are a good approximation for the electrons of the K shell, and there is good agreement between calculated and measured values of μ. Therefore, it appears unlikely that the discrepancy between experimental and calculated ($\Theta=315°$K) integrated intensities is a consequence of the calculated values of ϵ_0.

The error $\Delta\epsilon$ which is made by neglecting the contribution of the Compton and the thermal diffuse scattering to the absorption is given by

$$\Delta\epsilon=\frac{[(\mu_C)_0\epsilon-(\mu_C)_H]+[(\mu_{TDS})_0\epsilon-(\mu_{TDS})_H]}{\mu_{\mathrm{tot}}},$$

where μ_C and μ_{TSD} are, respectively, the Compton and thermal diffuse scattering corrections to the linear absorption coefficient; the suffixes 0 and H denote the average absorption coefficients and the dynamical absorption coefficient, respectively. μ_{tot} is the total linear absorption coefficient. The contributions to $\Delta\epsilon$ from Compton scattering may not be negligible, but since there is no theory on the dependence of $(\mu_C)_H$ on the scattering angle, in this paper we consider only the errors in ϵ due to thermal diffuse scattering contributions ($\Delta\epsilon_{TDS}$). The values of $(\mu_{TDS})_H$ which were calculated using the Einstein model of the vibrating crystal[10] are reported in Table V. In Table VI the $\Delta\epsilon_{TDS}$ are compared with $\Delta\epsilon_\Theta$, the latter being the difference in ϵ for the two Debye temperatures 300 and 315°K. This comparison was made because the ϵ values corresponding to $\Theta=300°$K gave intensity values in satisfactory agreement with the experimental results. It appears that the TDS contribution is appreciable for Cu $K\alpha$, but not for Mo $K\alpha$. However, since the precision of the calculated values for $(\mu_{TDS})_H$ and $(\mu_{TDS})_0$ cannot easily be assessed, it cannot be determined from this table if the contributions due to TDS are in fact negligible.

Values of the Debye temperature $\Theta=315°$K were previously determined from x-ray measurements of mean-square displacements on single crystals[24] and on powder samples of Cu[25,26] in the Bragg case. In addition, calculations of Θ from the frequency spectrum derived from phonon dispersion curves of Cu yielded $\Theta=317°$K for $T=295°$K,[27] in good agreement with the calculation of Debye-Waller factors from thermodynamic data.[28] The intensities of Table III were calculated with both $\Theta=315$ and 300°K since there is evidence for a lower "apparent" Debye temperature of Cu from experiments on the temperature dependence of anomalous transmission.[15,29,30] Liquid-nitrogen and room-temperature measurements on one sample 0.084 cm thick (crystal 1162) were made and the results are reported in Table VII. Both the absolute intensities at room temperature and the ratios R_{77}/R_{295} between the intensities at liquid nitrogen and room temperature confirm the fact that there is much better agreement with the values calculated for $\Theta=300°$K.

TABLE VI. Variations $(\Delta\epsilon)_\Theta$ of ϵ due to the use of two different Debye temperatures (300 and 315°K), and $(\Delta\epsilon)_{TDS}$ due to the contribution of thermal diffuse scattering at 295°K.

Reflection indices	$(\Delta\epsilon)_\Theta$	$(\Delta\epsilon)_{TDS}$ Cu $K\alpha$	$(\Delta\epsilon)_{TDS}$ Mo $K\alpha$
111	0.0031	0.0012	0.0004
200	0.0040	0.0016	0.0006
220	0.0078	0.0030	0.0007
222	0.0111	0.0040	0.0010

TABLE VII. Integrated intensities of crystal No. 1162 at room and liquid-nitrogen temperatures. Cu$K\alpha$ radiation reflected from a curved quartz monochromator. $hkl=111$.

T (°K)	Absolute integrated intensities×10^8 Experimental		Calculated Debye temperature 300°K		Calculated Debye temperature 315°K	
	R_H	R_T	R_H	R_T	R_H	R_T
77	125	136	131	138	136	143
295	52.5	55	53	55.9	60	63.3

	Relative integrated intensities×10^8 Experimental Reflected beam	Experimental Transmitted beam	Calculated Debye temperature 300°K	Calculated Debye temperature 315°K
$\frac{R_{77}}{R_{295}}$	2.38	2.47	2.47	2.26

The conclusion is that the discrepancy between the experimental data and those calculated with $\Theta=315°$K is to a good extent eliminated if the intensities are calculated with $\Theta_M=300°$K. This value agrees with the determination of the "apparent" Debye temperature of Cu through measurements of anomalous transmission intensities as a function of temperature. However, it cannot be concluded that the Debye temperature of Cu is 300°K rather than 315°K or vice versa, since thermal diffuse scattering and anharmonic contributions[31] to the "apparent" Debye temperature are difficult to evaluate.

No single parameter adjustment can make the calculated and experimental data agree perfectly, and probably in specific cases defects, thickness errors, etc., can account for some of the scatter in the data. Actually, considering the many approximations used

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in these calculations, it is encouraging that the agreement between theory and experiment is as good as it appears. It seems unlikely at present that further refinements of the calculations of ϵ_0 will improve the agreement between calculated and measured intensities. Precise calculations of the contributions of thermal diffuse scattering, Compton scattering, etc., to the Borrmann effect in copper may be more significant.

SUMMARY

Absolute values of integrated intensities in anomalous transmission have been measured for almost perfect Cu crystals varying in thickness from 0.014 to 0.22 cm. Mo $K\alpha$, Cu $K\alpha$, and Cr $K\alpha$ radiations were used with a double-crystal spectrometer for measuring the intensities of the 111, 200, 220, and 222 reflections. Relative and absolute values of integrated intensities in anomalous transmission and in the Bragg case for several reflections were measured with Ag $K\alpha$ and Mo $K\alpha$ radiations for a crystal containing 2×10^3 dislocation lines/cm^2.

Integrated intensities were calculated by means of the formulas of the dynamical theory of x-ray diffraction. For these calculations the dynamical values of the photoelectric absorption coefficients as a function of the scattering angle were computed by using formulas of the semiclassical theory of absorption of radiation. Two Debye temperatures, 315 and 300°K, were used for the evaluation of the Debye-Waller factor. For $\Theta=300$°K, the calculated intensities are in better agreement with the experimental ones, and there is some experimental justification for this value of the Debye temperature. These results should not be taken as proof that the Debye temperature of Cu is 300°K rather than 315°K. Apart from the above minor discrepancies, the agreement of the experimental intensities with those calculated by applying the dynamical theory of diffraction is satisfactory.

For $\Theta_M=315$°K, the generally accepted value, calculated intensities were systematically higher than experimental ones. This work shows clearly that there are a number of factors, such as (1) the thickness and the strain (or the defects) of the crystal, (2) the exact value of the "apparent" Debye temperature, and (3) other x-ray scattering effects which should be taken into consideration for any significant comparison between calculated and measured values of intensities diffracted in anomalous transmission.

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Thermopower of Pure Aluminum*

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The thermopower of 99.999% pure, polycrystalline aluminum has been measured from 4.2 to 300°K using Pb as the standard, and from 300 to above 700°K using Au and Cu as alternative standards. The thermopower is negative at all temperatures with a phonon-drag peak occurring at about 75°K. From 200 to 300°K the thermopower S is well-described by the relation $S=-2.34\times10^{-3}T-284/T$ μV/°K. The thermopowers determined against Au and Cu are not quite the same above 450°K, showing a difference of about 0.1 μV/°K at 700°K. However, each set of data is consistent with the form $S=-AT-B/T$ (A and B are positive constants); and a reasonable average for the two standards is given by $S=-3.00\times10^{-3}T-229/T$ μV/°K, for $T>300$°K. These two terms are interpreted as representing diffusion thermopower and phonon-drag thermopower contributions, respectively. If this interpretation is correct, it represents the first clear example of a nonzero phonon-drag thermopower in a metal at temperatures above 300°K.

INTRODUCTION

It is generally assumed that the thermopower S of very pure, simple metals can be described as the sum of two terms: a diffusion contribution S_e associated with the spatial redistribution of conduction electrons in the necessary temperature gradient, and a phonon-drag contribution S_g arising from the interaction between the electrons and the nonequilibrium part of the phonon distribution produced by this temperature gradient. S_e and S_g, in turn, contain contributions from two types of electron-phonon interaction: normal electron-phonon scattering, in which the total crystal momentum of the incoming electrons and phonons is transferred undiminished to the outgoing electrons and phonons; and umklapp scattering, in which some crystal momentum is given to the crystal lattice (a reciprocal lattice vector

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