PHYSICAL REVIEW B VOLUME 4, NUMBER 6 15 SEPTEMBER 1971

Effect of Temperature on the Anomalous Transmission of X Rays in Copper and Zinc

C. Ghezzi
Istituto di Fisica dell'Università, Parma, Italy

and

A. Merlini and S. Pace
Solid State Physics, Physics Division, C. C. R. Euratom, Ispra, Italy

(Received 2 February 1971)

Absolute values of integrated intensities, diffracted in anomalous transmission through two nearly perfect single crystals of Cu and Zn, were measured with Cu $K\alpha$ radiation for the {220} reflection of Cu ($\mu_0 t \approx 23$) and for the {0002} reflection of Zn ($\mu_0 t \approx 21$), in the temperature interval 0–120 °C. The temperature dependence of the diffracted intensities, which was investigated for various positions of the incident beam on the surface of the crystals, did not vary with the local degree of crystal perfection. The Debye temperature was determined from the temperature dependence of the diffracted intensities. For Cu it was found that $\Theta = 306 \pm 4$ °K when corrected for the contribution of Bragg scattering to the experimental value of the average absorption coefficient, for the contributions of phonon scattering to the average and dynamical absorption coefficients, and for the anharmonic effects on the Debye-Waller factor. The above figure is in satisfactory agreement with the Debye temperatures obtained from other anomalous-transmission experiments and from vibrational frequency spectra determined with neutron-inelastic-scattering experiments. In the case of Zn, the Debye temperature for the *c* component of the mean-square vibration displacement was 166 ± 4 °K in good agreement with a previously published result. Values of Θ for Si and Ge crystals, obtained from anomalous-transmission experiments by various authors, are briefly reviewed and the effects of phonon-scattering contributions to the average and dynamical absorption coefficients are estimated.

I. INTRODUCTION

There are a number of experimental studies on the temperature dependence of the intensities diffracted in anomalous transmission (Borrmann effect) through nearly perfect crystals. In agreement with theory, the experiments indicate that the diffracted intensities depend on temperature through a Debye-Waller factor of the imaginary part of the atomic scattering factor. This Debye-Waller factor is equal to that of the real part of the atomic scattering factor, if the absorption of the x rays is due to the photoelectric effect. However, the Debye temperatures obtained from experiments in anomalous transmission are, as a rule, slightly smaller than those calculated on the basis of phonon frequency spectra or derived from experimental x-ray data in the Bragg case. A good example of these discrepancies is given by the data available for nearly perfect copper crystals. Anomalous-transmission experiments on these crystals show that the values of Θ obtained from the temperature dependence of the intensities,[1,2] or used to match the absolute values of the calculated and experimental intensities,[3] are from 10 to 20 °K smaller than the generally accepted value. The theory shows that there are small contributions from phonon scattering to the average and dynamical absorption coefficients. These contributions, which have a temperature dependence different from the photoelectric part of the absorption, might account for the abovementioned differences in the values of Θ.

The purpose of the present work, some results of which were previously presented in abstract form,[1] is the experimental determination of Θ from measurements of intensities diffracted through thick crystals of Cu and Zn. The effect of lattice perfection on the temperature dependence of the diffracted intensities was investigated and the various factors which can influence the determination of Θ were also analyzed.

II. EXPERIMENTAL PROCEDURE

The experimental method for the measurements of integrated intensities was mainly the one described in previous papers.[4,5] The crystal, placed on the focal line of a curved quartz monochromator, was oriented for diffraction on planes perpendicular to the surface of the crystal (symmetrical Laue case). The intensities of the {220} and {0002} reflections were measured for Cu and Zn crystals, respectively. Cu $K\alpha$ radiation was used in all experiments. The integrated intensities of the transmitted and the reflected beams were measured by rotating the crystal through the whole angular interval of the diffracted rays. Two NaI scintillation counters with single-channel pulse-height analyzers were used as detector and monitor. Care was taken in order to avoid any contribution of short-wavelength harmonics (the x-ray tube was operated at about 45 kV) to the intensities of the incident beam and of the beams diffracted in anomalous transmission. The absolute values of the intensities were obtained by measuring the incident-beam intensity which was reduced by calibrated Ni filters. An accuracy better than ± 1% was achieved in the relative integrated intensity measurements, and better than ± 5% in absolute measurements. The temperature of the sample was varied from 0 to about 120 °C, and was measured with an accuracy better than ± 0.5 deg. The crystal was kept vertical in a metal frame by thin metal springs within a chamber of the furnace which contained a helium atmosphere. In this way, elastic deformations and lattice strains due to thermal gradients were avoided. The crystal and the furnace were translated with respect to the incident beam by means of two orthogonal slides. In this way it was possible to measure the diffracted intensities for various positions of the incident beam on the surface of the same crystal. The thickness of the crystal was measured by using a sensitive capacitance bridge with an accuracy of ± 2 μ; and, thus, any plastic deformation of the metal sample was avoided. Since different parts of each crystal had different degrees of lattice perfection and slightly different thicknesses, great care was taken to determine the thicknesses of the zones corresponding to the x-ray intensity measurements. The thickness was taken as equal to the arithmetic mean of many measurements done inside the area (0.1 mm wide×2.5 mm high, equal to the x-ray beam section at the surface of the sample) of each zone. This procedure was repeated for all the parts of the crystal which were investigated with the x rays.

III. EXPERIMENTAL RESULTS

First, the integrated intensities of both the reflected and transmitted beams were measured as a function of the position of the incident beam on the surface of the crystal. The absolute values of the measured intensities were then compared with the calculated values (the procedure followed for the calculation will be explained below). A "degree of perfection" α, which was defined as the ratio between the experimental and the calculated values, was assigned to each zone of the crystal. Some of these zones, with various thicknesses and different values of α, were selected in order to be studied in the temperature range 0–120 °C. An important criterion for the above-mentioned selection was the photograph of the diffracted beams. Pictures of the reflected and transmitted beams were taken with the crystal in the diffracting position. Only those zones of the crystal for which the pattern of the beam was made of a single line, fairly uniform in intensity along its length, were further investigated. The procedure was followed with both the copper and zinc crystals.

The characteristics of the crystal zones on which the intensities were measured as a function of temperature are summarized in Tables I and II for the {220} reflection in copper and for the {0002} reflection in zinc, respectively. The positions of the incident beam on the surface of the crystal are indicated with capital letters. The thickness and the degree of perfection α of each one of the two diffracted beams are also reported. Information on whether the intensity measurements were done for the transmitted beam only or for both diffracted beams is given in the last column of the tables.

It should be noted that in copper, α was nearly the same for both the reflected and transmitted beams in all the positions (Table I). That is, the ratio R_T/R_H of the intensities of the diffracted beams was that expected for a perfect crystal. For the position B of zinc instead, the value of α for the transmitted beam was almost double that of the reflected beam (Table II); this zone of the crystal, however, had a very low degree of perfection.

Figures 1 and 2 show typical plots of the log of the intensity vs temperature. In the case of copper (Fig. 1), the experimental data correspond to the transmitted beam for the A and C zones (Table I) of the crystal. The same crystal thickness, but a different degree of perfection, corresponds to these zones. For zinc, the experimental values of the intensities of the transmitted and reflected beams for the B zone (Table II) are reported in Fig. 2.

Approximate values of the Debye temperature

TABLE I. Summary of the intensity measurements on a copper crystal, as a function of temperature. Measurements were done for the transmitted beam or for both diffracted beams, as explained in the last column.

Zone of the crystal	Thickness (mm)	$\mu_0 t$	Degree of perfection Transmitted beam	 Reflected beam	Beam intensity measurements
A	0.405 ± 0.003	22.29	0.91	0.90	Transmitted
B	0.457 ± 0.003	25.15	0.82	0.79	Both beams
C	0.405 ± 0.003	22.29	0.71	0.71	Transmitted
D	0.419 ± 0.003	23.06	0.56	0.57	Transmitted

TABLE II. Summary of the intensity measuements on a zinc crystal, as a function of temperature. The measurements were done on the transmitted beams or on both beams, as explained in the last column.

Zone of the crystal	Thickness (mm)	$\mu_0 t$	Degree of perfection Transmitted beam	 Reflected beam	Beam intensity measurements
A	0.480 ± 0.003	20.71	0.47	0.47	Transmitted
B	0.488 ± 0.003	21.06	0.22	0.13	Both beams
Ref. 4	0.620	26.75	0.71	0.70	Both beams

were obtained from the experimental data by means of the approximate expression

$$\Theta = \left(\frac{(6h^2/mk)\,(\frac{1}{2} + \mu_0 t \epsilon_0)}{|d \ln R/dT|}\right)^{1/2} \frac{\sin\theta}{\lambda} , \tag{1}$$

where h and k are Planck's and Boltzmann's constants, respectively; R is the integrated intensity; m is the atom mass; μ_0 is the average absorption coefficient; ϵ_0 is the ratio between the imaginary parts of the structure factors for the reflected and incident beams, respectively; t is the thickness of the crystal in the direction of the incident x-ray beam; θ is the Bragg angle for the wavelength λ of the incident radiation.

The expression of the integrated intensities of the reflected (H) and transmitted (T) beams is

$$R_{H(T)} = \text{const}\,|F_H|\, e^{-\mu_0 t} \cosh(\mu_H t)\, \Phi_{H(T)}(\mu_H t) , \tag{2}$$

where F_H is the structure factor for the reflection $H \equiv h,\ k,\ l$; t is the thickness of the crystal, as explained for formula (1); μ_0 and μ_H are the average and dynamical absorption coefficients, respectively; $\Phi_{H(T)}(\mu_H t)$ are functions which vary slowly with the thickness of the crystal and can be approximated by $2(\pi/8\mu_H t)^{1/2}$ for $\mu_H t$ greater than 20.[6] Formula (2) depends on temperature because μ_H is a function of T, as explained below, and F_H contains the Debye-Waller factor e^{-M}, where

$$M = \left(\frac{\sin\theta}{\lambda}\right)^2 \frac{6h^2}{mk\Theta} \left[\frac{1}{4} + \frac{T}{\Theta}\, \zeta\!\left(\frac{\Theta}{T}\right)\right] ,$$

$\zeta(\Theta/T)$ being the Debye function.

The Debye temperature was determined with a precision greater than that obtained from formula (1) by means of a computer. Different Debye temperatures, close to the approximate value previously determined, were inserted in formula (2); then, the Debye temperature for which the calculated cruve was parallel to the experimental one was chosen.

For the numerical calculation of formula (2), the values of μ_0 were determined by measurements of the intensity of the Cu $K\alpha$ radiation (monochromatized by a curved quartz monochromator) transmitted through polycrystalline sheets of Cu and Zn. It was found that the absorption coefficient μ_{0P} of the polycrystalline sheet was $439 \pm 6\ \text{cm}^{-1}$ for Cu, a value which differs by less than 2% from that al-

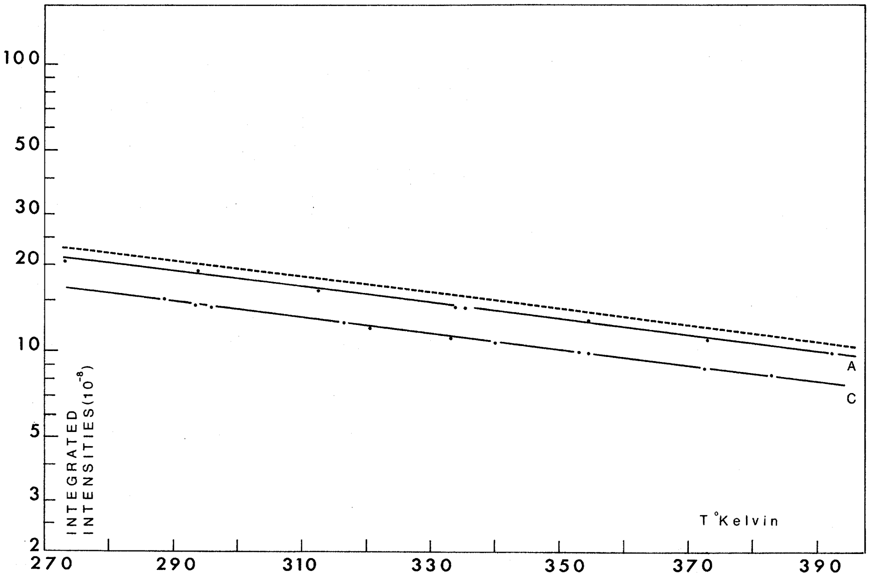

FIG. 1. Logarithm of the integrated intensity of the transmitted beam versus temperature for the {220} reflection of a copper crystal. The experimental points correspond to two regions of the crystal of equal thickness but of different perfection. The dashed line is the plot of the values calculated for Θ = 306 °K. The phonon-scattering contribution to the absorption coefficient and the anharmonic terms of the Debye-Waller factor were included in the calculation, as explained in the text.

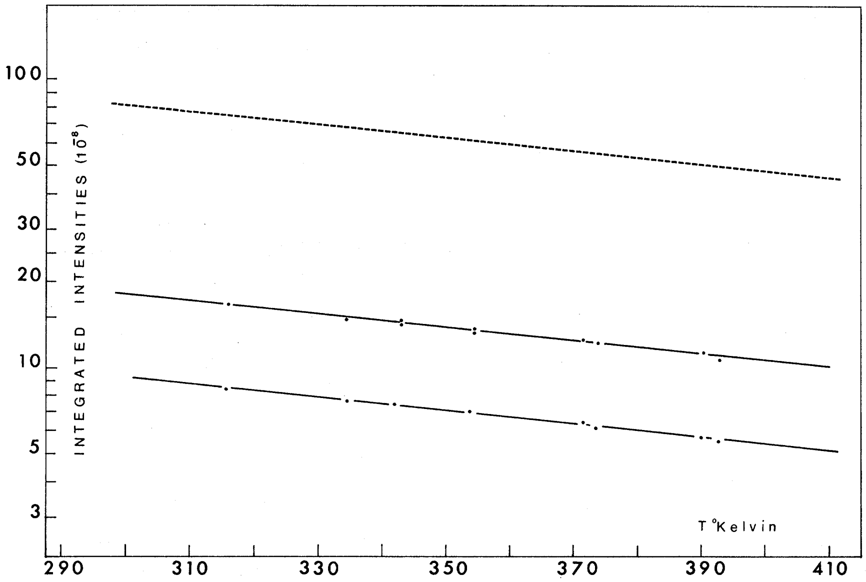

FIG. 2. Logarithm of the integrated intensity of the transmitted and reflected beams for the {0002} reflection of a Zn crystal. Upper and lower experimental points refer to the transmitted and reflected beams, respectively. The dashed line corresponds to the values calculated for $\Theta = 163$ °K: the phonon-scattering contribution to the absorption coefficient was not included in the calculation.

ready published.[3] For Zn, $\mu_{0P} = 410 \pm 7$ cm^{-1}, which is in full agreement with the previously reported value.[4] In the case of Cu, the value of μ_0 used in formula (2) was the above-mentioned figure less the contribution μ_{BS} of the Bragg scattering to the absorption of the polycrystalline sheet. This contribution was evaluated by means of the formula (B1), as explained in Appendix B. μ_{BS} was taken equal to 0 for Zn because the expression (B1) is valid only for cubic crystals.

The average absorption coefficient μ_0 of a single crystal is made of three different contributions:

$$\mu_0 = (\mu_{PE})_0 + (\mu_{TDS})_0 + (\mu_C)_0 \ .$$

The first contribution $(\mu_{PE})_0$ which is by far the most important for the x-ray wavelengths used in diffraction, is due to photoelectric absorption. The second and the third are the contributions due to phonon and Compton scatterings, respectively. The Compton contribution is too small to have any appreciable effect in the cases described in this study, and therefore will not be considered any further. The contribution due to phonon scattering is made of two parts:

$$(\mu_{TDS})_0 = \mu_0^{ES} + \mu_0^C \ . \tag{3}$$

μ_0^{ES} is the scattering contribution calculated by using a model in which the oscillations of the various atoms are independent (Einstein theory of the vibrating crystal). The expression used to calculate μ_0^{ES} is given by formula (A1) in Appendix A and the calculated values of μ_0^{ES} for the reflections {111} and {220} of Cu and of {0002} of Zn, at $T = 295$ °K, are reported in Table III together with data concerning other crystals of interest. μ_0^C is the contribution due to pair correlations among the vibrating atoms and was calculated by means of formula (A3) also reported in Appendix A (see Table IV).

The dynamical absorption coefficient μ_H is made of two parts,

$$\mu_H = (\mu_{PE})_H + (\mu_{TDS})_H \ ,$$

due to photoelectric absorption and phonon scattering, respectively. The photoelectric part $(\mu_{PE})_H$ can be written as

$$(\mu_{PE})_H = (\mu_{PE})_0 \epsilon_0 e^{-M} \ , \tag{4}$$

where e^{-M} is the Debye-Waller factor.

$(\mu_{PE})_0$ was obtained by subtracting $(\mu_{TDS})_0$ (and μ_{BS} in the case of Cu) from the absorption coefficient μ_{0P} of the polycrystalline sheet. The values of ϵ_0 (for the component of the radiation with per-

TABLE III. Contribution of the noncorrelated (Einstein) part of the x-ray thermal diffuse scattering to the average μ_0^{ES} and dynamical μ_H^{ES} absorption coefficients in cm^{-1}, at $T = 295$ °K. Only the contribution of the perpendicularly polarized component of the radiation is given.

Crystal	λ	μ_0^{ES}		μ_H^{ES}	
			{220}	{400}	{400}
Si	Cu $K\alpha$	0.24	0.19	•••	•••
Ge	Cu $K\alpha$	1.42	1.15	0.91	0.48
	Mo $K\alpha$	1.52	1.40	1.29	1.09
			μ_H^{ES}		
		μ_0^{ES}	{111}	{220}	
Cu	Cu $K\alpha$	1.68	1.37	0.92	
		μ_0^{ES}	μ_{0002}^{ES}		
Zn	Cu $K\alpha$	6.09	5.11		

TABLE IV. Contribution of the atom-pair correlations of x-ray phonon scattering μ_0^C to the average absorption coefficient, in cm^{-1}, at $T = 295$ °K. The contribution of the perpendicularly polarized component of the radiation only is given.

		μ_0^C			
Crystal	λ	{111}	{220}	{400}	{440}
Si	Cu $K\alpha$	•••	0.031	•••	•••
Ge	Cu $K\alpha$	•••	0.17	0.24	0.27
	Mo $K\alpha$	•••	0.042	0.061	0.072
Cu	Cu $K\alpha$	0.54	0.76	•••	•••

pendicular polarization, the only one of interest in this work) were taken equal to 0.9820 for the {220} reflection of Cu[3] and to 0.9970 for the {0002} reflection of Zn.[4] The phonon contribution $(\mu_{\mathrm{TDS}})_H$ is equal to μ_H^{ES} [see formula (A2), in Appendix A and the results of the calculations at $T = 295$ °K in Table III], because μ_H^C (the part due to pair correlations) is, to a good approximation, equal to 0.[7]

An anharmonic correction ΔM to the exponent M of the Debye-Waller factor of Cu was also introduced in the program for the calculation of the integrated intensity. The expression of ΔM is given by formula (8), as explained in the Discussion.

The value obtained for the Debye temperature of Cu was $\Theta = 306 \pm 4$ °K with the above-mentioned corrections and in all the cases which were investigated (see Table I). By taking $\mu_0 = 439\ \mathrm{cm}^{-1}$, with no corrections for the phonon and Bragg scatterings and for the anharmonic effects, it was found that $\Theta = 296$ °K by machine calculations and $\Theta \approx 319$ °K by applying the approximate formula (1).

In the case of Zn, $\Theta = 166 \pm 4$ °K for all the cases reported in Table II. It was found that $\Theta = 163$ °K with no corrections for phonons scattering and $\Theta = 170$ °K from the approximate formula (1) in full agreement with the value previously published.[4] It is important to stress that the determined values of the Debye temperature for both Cu and Zn did not depend on the degree of perfection of the investigated zone of the crystals.

IV. DISCUSSION

The various factors which can affect the determination of the Debye temperature will now be discussed. The approximate slopes of the curves shown in Figs. 1 and 2 are obtained by derivation of formula (2) with $(\mu_{\mathrm{PE}})_H/\mu_H \approx 1$ and $e^{-M} \approx 1 - M$:

$$\frac{d\ln R}{dT} = -\left[(\mu_{\mathrm{PE}})_0\epsilon_0 t + \tfrac{1}{2}\right]\frac{dM}{dT} - t\,\frac{d[(\mu_{\mathrm{TDS}})_0 - (\mu_{\mathrm{TDS}})_H]}{dT}\ . \tag{5}$$

The determination of Θ is affected [see formula (1)] by the values of μ_0, μ_H, and ϵ_0, by anharmonic contributions to M, and by the measurement of the thickness t of the crystal. A precision greater than 1% in the determination of t, as is usually the case, affects the value of Θ by less than 0.5%. As far as ϵ_0 is concerned, it is unlikely that the approximations made for the calculation of ϵ_0 have any appreciable effect on Θ (see the discussion in Ref. 3). The other quantities μ_0, μ_H, and M are considered below in detail. First, $(\mu_{\mathrm{PE}})_0$ is separated from the total absorption coefficient μ_0, since its effect on the value of Θ can be estimated immediately. The effects of $(\mu_{\mathrm{TDS}})_0$, $(\mu_{\mathrm{TDS}})_H$, and M are, instead, calculated through their modification of the slope $d\ln R/dT$. From (1) and (5) it follows that

$$\Delta\Theta/\Theta = \tfrac{1}{2}[\Delta(\mu_{\mathrm{PE}})_0/(\mu_{\mathrm{PE}})_0 + \Delta x/x]\ , \tag{6}$$

where $x = |d\ln R/dT|$.

Effect of Errors in the Value of μ_0

The value $(\mu_{\mathrm{PE}})_0$ is often taken equal to the values of absorption coefficients μ_0 found in the tables or in the literature. Since these values often vary by a few percent, their effect on the determination of Θ is not negligible. When the absorption coefficient is measured by means of a transmission experiment on a polycrystalline sample, the contribution μ_{BS} of Bragg scattering—and, strictly speaking, also the contribution of $(\mu_{\mathrm{TDS}})_0$—should be subtracted from the measured value. In the case of the present work, the value of μ_{BS} for Cu was calculated as explained in Appendix B. Since $\mu_{\mathrm{BS}} = 9.54\ \mathrm{cm}^{-1}$ the value of Θ obtained by taking $\mu_0 = 439\ \mathrm{cm}^{-1}$ should be decreased by about 3 °K.

Effect of the Contributions of Phonon Scattering to the Absorption Coefficient

The expression of $\Delta x/x$ in (6) follows from (5):

$$\frac{\Delta x}{x} = \frac{d[(\mu_{\mathrm{TDS}})_0 - (\mu_{\mathrm{TDS}})_H]}{dT}\bigg/\left((\mu_{\mathrm{PE}})_0\epsilon_0 + \frac{1}{2t}\right)\frac{dM}{dT}\ , \tag{7}$$

where $(\mu_{\mathrm{TDS}})_0 = \mu_0^{\mathrm{ES}} + \mu_0^C$ and $(\mu_{\mathrm{TDS}})_H \approx \mu_H^{\mathrm{ES}}$. The values of μ_0^{ES}, μ_H^{ES}, and μ_0^C for Si, Ge, Cu, and Zn at various temperatures were calculated by means of a computer (with the exception of μ_0^C for Zn), for the reflections *hkl* of interest. For Zn the values of μ_0^{ES} and μ_H^{ES} are merely demonstrative because the crystal was assumed to have an isotropic Θ equal to that corresponding to the basal planes. The calculated values of μ_0^{ES} and μ_H^{ES} at $T = 295$ °K are reported in Table III and those of μ_0^C in Table IV. The calculations were done for the perpendicularly polarized radiation, which is the only important radiation for diffraction in anomalous transmission. The temperature derivatives which appear in (7) were obtained by numerical derivation of the above-calculated data and they are reported in Table V for $T = 295$ °K. The value of $d(\mu_0 - \mu_H)^{\mathrm{ES}}/dT$, which is roughly proportional to the square of the x-ray radiation wavelength, is

TABLE V. Contribution of the phonon scattering (for the perpendicularly polarized component of the radiation) to the slope of the log of the integrated intensity versus temperature, at $T = 295\,^\circ\mathrm{K}$ and for unit thickness of the crystal. Both the contributions of the noncorrelated part and of the atom-pair correlations are given for Si, Ge, and Cu. The contribution of the noncorrelated part only is given for Zn.

			$d(\mu_0 - \mu_H)^{\mathrm{ES}}/dT\ (10^3)$				$d\mu_0^C/dT\ (10^3)$		
Crystal	λ	{111}	{220}	{400}	{440}	{111}	{220}	{400}	{440}
Si	Cu $K\alpha$	•••	0.13	•••	•••	•••	0.095	•••	•••
Ge	Cu $K\alpha$	•••	0.85	1.59	2.80	•••	0.54	0.71	0.67
	Mo $K\alpha$	•••	0.41	0.78	1.39	•••	0.13	0.18	0.18
Cu	Cu $K\alpha$	0.99	2.34	•••	•••	1.69	2.15	•••	•••
		{0002}							
Zn	Cu $K\alpha$	3.25							

approximatively constant at room temperature (there is an increase at low temperatures and a slow decrease at high temperatures) and increases with the order of the reflection. The derivative of μ_0^C is roughly equal to $\mu_0^C e^{-2M}/T$ for $T \geq \Theta$ and M small. In the case of Cu, the corrections $\Delta\Theta$ due to the noncorrelated part of phonon scattering are about 3.5 and 3 °K, respectively, for the {111} and {220} reflections, with Cu $K\alpha$ radiation. The corrections $\Delta\Theta$ due to the correlated part μ_0^C of phonon scattering are +5.5 and +2.5 °K for the {111} and {220} reflections, respectively.

Anharmonic Contributions to the Debye-Waller Factor

As mentioned above, anharmonic contributions to the Debye-Waller factor may have an appreciable effect on the apparent value of Θ. Cubic- and quartic-anharmonic contributions to the Debye-Waller factor were evaluated in the "high-temperature" limit by Maradudin and Flinn for a fcc lattice.[8] Only the isotropic-anharmonic correction to the mean-square amplitude of the atom's vibration will be considered here. These corrections which are proportional to the square of the absolute temperature are labeled M_1, M_2, and M_0 (TEC), where the last one is the effect of the thermal expansion of the crystal (TEC). The other correction terms (M_3 and M_4) which are proportional to the cube of the absolute temperature give a contribution smaller than the 10% of the contribution of the above-mentioned terms at the melting temperature of lead. They can then be reasonably neglected at the moderate temperatures of the present work in copper which has a Debye temperature considerably greater than lead.

By using a nearest-neighbor central-force model, M_1, M_2, and M_0 (TEC) can be expressed in terms of the derivatives of the potential energy of interaction $\phi(r_0)$ between nearest neighbors,[8] as follows:

$$M_1 = -0.0524 \frac{4\pi^2 S^2}{\lambda^2} (kT)^2 \frac{\phi^{\mathrm{IV}}(\bar{r}_0)}{[\phi^{\mathrm{II}}(\bar{r}_0)]^3} ,$$

$$M_2 = 0.021115 \frac{4\pi^2 S^2}{\lambda^2} (kT)^2 \frac{[\phi^{\mathrm{III}}(\bar{r}_0)]^2}{[\phi^{\mathrm{II}}(\bar{r}_0)]^4} ,$$

$$M_0(\mathrm{TEC}) = 0.0524 \frac{4\pi^2 S^2}{\lambda^2} (kT)^2 \frac{[\phi^{\mathrm{III}}(\bar{r}_0)]^2}{[\phi^{\mathrm{II}}(\bar{r}_0)]^4} .$$

$\bar{r}_0$ is related to the equilibrium value r_0 of the nearest-neighbor separation at temperature T by

$$r_0 = (1+\delta)\bar{r}_0 ,$$

where δ is the linear expansivity of the lattice. $\phi(r_0)$ is assumed to be a Morse-type potential in order to obtain its fourth derivative

$$\phi^{\mathrm{IV}}(\bar{r}_0) = \tfrac{7}{9}[\phi^{\mathrm{III}}(\bar{r}_0)]^2/\phi^{\mathrm{II}}(\bar{r}_0)$$

and use is made of the expression of δ in the high-temperature limit

$$\delta = -(kT/4\bar{r}_0)\,\phi^{\mathrm{III}}(\bar{r}_0)/[\phi^{\mathrm{II}}(\bar{r}_0)]^2 .$$

By combining all the above formulas, the simple expression ΔM, valid in the high-temperature limit, of the total anharmonic correction follows:

$$\Delta M = M_1 + M_2 + M_0(\mathrm{TEC})$$

$$= 0.03276\ 4\pi^2 S^2 \lambda^{-2} (4\bar{r}_0\beta)^2 T^2 , \tag{8}$$

where $\beta = d\delta/dT$ is the linear expansion coefficient. The correction ΔM of the Debye-Waller factor, with the numerical values $\bar{r}_0 \approx r_0 = 2.556$ Å and $\beta = 1.708 \times 10^{-5}$ (average value in the range between 0 and 150 °C), was inserted in the program to compute the integrated intensity in anomalous transmission, and was also used to estimate the $\Delta\Theta$ due to the anharmonic contributions, by means of formula (6). It was found that $\Delta\Theta = 8\,^\circ\mathrm{K}$ for Cu at $T = 295\,^\circ\mathrm{K}$. This correction is in satisfactory agreement with that obtained by using the formulation of the temperature dependence of Θ in terms of the Grüneisen constant and of the lattice volume.[9] In fact, the thermal expansion of the lattice is responsible for the greatest part of ΔM, because the terms M_1 and M_2 partially cancel each other.

TABLE VI. Summary of Debye temperature values obtained through measurements of intensities diffracted in anomalous transmission. The values of the Debye temperature in the left side of the fifth column are those given by the respective authors. In the right side of the same column the above values are corrected as explained in the text.

Crystal	Reflection	Radiation	Temp. range (°K)	Θ (°K) From literature	 Corrected	Refs.
Si	$\{220\}$	Cu $K\alpha$	100–650	535 at 300 °K	535 at 300 °K	10
Ge	$\{220\}$ $\{400\}$	Cu $K\alpha$	230–700	295 ± 5	298 ± 5	13
	$\{220\}$ $\{400\}$ $\{422\}$	Cu $K\alpha$	300–375	290	294	14
	$\{220\}$	Cu $K\alpha$ Mo $K\alpha$	80–500	283 ± 3	286 ± 3	5
	$\{220\}$	Cu $K\alpha$	85–650	296 at 300 °K	296 at 300 °K	15
	$\{220\}$ $\{400\}$ $\{440\}$	Mo $K\alpha$	5–293	290	292	16
Cu	$\{111\}$	Cu $K\alpha$	77–377	306 ± 4	319 ± 4	2
	$\{220\}$	Cu $K\alpha$	273–393	296 ± 4	306 ± 4	This work
Zn	$\{0002\}$	Cu $K\alpha$	80–525	170 ± 3	166 ± 4	4
	$\{0002\}$	Cu $K\alpha$	273–393	163 ± 4	166 ± 4	This work

Comparison of the Debye Temperatures Obtained from Experiments in Anomalous Transmission

In Table VI we have reported the values of Debye temperatures obtained from experiments in anomalous transmission for Si, Ge, Cu, and Zn, together with the x-ray radiation used, the reflections, and the range of temperatures investigated. In the left side of the fifth column of the table the values of the Debye temperatures are listed as given by the authors. In the right side of the same column, the above-mentioned values were corrected for the contributions of phonon scattering to the absorption coefficient. As explained above, the Debye temperature of Cu was also corrected for the contribution of the Bragg scattering to the measured absorption coefficient and for the anharmonic effects on the Debye-Waller factor. The anharmonic effects can be neglected in the case of Si and Ge, as shown by the application of the formula due to Paskin.[9] Anharmonic corrections should be important in the case of Zn, but the formulas available are valid only for cubic crystals.

Silicon. The temperature dependence of the intensities diffracted in anomalous transmission for the $\{220\}$ reflection was investigated with Cu $K\alpha$ by Kyutt and Efimov, who determined the variation of the intensities on the thickness of the crystal at various temperatures.[10] The effect of phonon-scattering contributions to the absorption coefficients was taken into account and yields a correction $\Delta\Theta \approx 30$ °K at room temperature. It must also be noted that Kyutt and Efimov took $\mu_0 = 146$ cm^{-1}, in agreement with $\mu_0 = 144$ cm^{-1} measured on a single-crystal lamella of Si.[11] The most reliable value of the average absorption coefficient of Si is probably that calculated by using the formulas reported in a previous work.[3] If the calculated value $\mu_0 = 141$ cm^{-1} (which includes the photoelectric and Compton contributions) is taken, Θ is equal to 526 °K at $T = 295$ °K, a value which is about 3% smaller than $\Theta = 543$ °K found with polycrystalline samples of Si.[12]

Germanium. The corrected values of Θ from the works of various authors do not differ by more than 4%. If an average value of Θ is taken, this will agree with the Debye temperature calculated by using the vibrational frequency spectrum obtained from neutron inelastic scattering experiments.[12]

Copper. The two corrected Debye temperatures in Table VI are not directly comparable because they were determined by using two slightly different values of the average absorption coefficient μ_0. If the same μ_0 is used in both cases, the two values of Θ differ by less than 4%.[17] Baldwin[2] has determined Θ from intensity measurements taken in a vast temperature range (77–377 °K) and for three crystals of different thicknesses.[18] For the thinnest one ($\mu_0 t = 20.4$) of the three samples, he found $\Theta = 305 \pm 12$ °K by applying an approximate formula which introduces non-negligible errors for such a thickness (the same formula is, instead, precise enough for the other two crystals with $\mu_0 t > 50$). When the above-mentioned formula is applied to the experimental results of this work, it is found that $\Theta = 307 \pm 5$ °K (instead of $\Theta = 296$ °K) in good agreement with the results of Baldwin.

In a previous study, a satisfactory agreement was found between experimental and calculated values of intensities diffracted in anomalous transmission at room temperature by using an "apparent" Debye temperature equal to 300 °K.[3] When this figure is corrected for the anharmonic effects [see formula (8)] and for the contributions of phonon scattering to the absorption coefficients, the value of Θ is 312 °K. $\Theta = 314$ °K,[19] and 317 ° K[20] are the Debye temperatures calculated from vibrational frequency spectra which were obtained from neutron-inelastic-scattering experiments at room temperature. These values of Θ must be corrected for the thermal expansion of the lattice in order to compare them with the corrected values of Table VI. An estimate of this correction can be obtained by using the term M_0 (TEC) in formula (8) or the Paskin formula,[9] and amounts to about 5 °K.[21] Finally, the values of Θ obtained from x-ray diffraction measurements on powders[22, 23] and on single crystals[24] are in the range 307–327 °K. These last values should also be corrected for the anharmonic contributions to the Debye-Waller factor; as mentioned before, such a correction amounts to $\Delta\Theta = 8$ °K at $T = 295$ °K for measurements of intensities versus temperature.

Zinc. The difference between the two uncorrected figures of the Debye temperature (see Table VI) is due to the approximate formula which was used to calculate Θ in the previous study.[4] In fact, there is complete agreement between the experimental results of the present and previous works. As already mentioned, the formulas used to calculate μ_0 and μ_H^{ES} are not valid for a hexagonal crystal. However, the contributions of Bragg and phonon scatterings to the absorption coefficients should yield only a small correction, about equal to that used in Table VI.

V. CONCLUSIONS

The temperature dependence of the integrated intensities, diffracted in anomalous transmission, was measured for the $\{220\}$ reflection of a crystal of Cu ($\mu_0 t \approx 23$) and for the $\{0002\}$ reflection of a crystal of Zn ($\mu_0 t \approx 21$), in the temperature range 0–120 °C. These measurements were repeated for various positions of the incident beam on the surface of the single crystal. The local degree of perfection of the crystal did affect the absolute value of the integrated intensity, but it did not influence the temperature dependence of the intensity.

The determination of the Debye temperature from the variation of the anomalous-transmission intensities with temperature can be affected by (a) the value used for the average absorption coefficient which is usually obtained from the attenuation of the x rays by a polycrystalline sample, and by (b) the contributions of phonon scattering to the average and dynamical absorption coefficients. As in the Bragg case, the Debye temperature must also be corrected for the anharmonic contributions to the Debye-Waller factor. The Debye temperature of Cu, corrected for all the above-mentioned effects, was found to be equal to 306 ± 4 °K. This figure should be compared with the corrected values 319 ± 4, 312, and 320 °K obtained from other anomalous-transmission measurements as a function of temperature,[2] from the comparison between experimental and calculated intensities in anomalous transmission,[3] and from neutron-inelastic-scattering data,[19,20] respectively. The agreement can be considered satisfactory, although the difference among the various values is somewhat greater than the experimental error.

In the case of Zn, the value of the Debye temperature was 166 ± 3 °K, in good agreement with previous results.[4]

ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance and the contribution of Dr. L. Ragnotti, who made available some measurements on Zn crystals. Thanks are due Dr. F. W. Young, Jr. (Solid State Division ORNL) who kindly gave us the Cu crystal.

APPENDIX A: CALCULATION OF THE CONTRIBUTIONS OF PHONON SCATTERING TO THE AVERAGE AND DYNAMICAL ABSORPTION COEFFICIENTS

The formulas used to calculate the contributions μ_0^{ES} and μ_H^{ES} to the average and dynamical absorption coefficients were obtained by Hall and Hirsch[25] in the case of the Einstein model for a vibrating crystal and by Dederichs[7] and by Afanas'ev and Kagan[26] in the general case. These formulas in the case of perpendicular polarized radiation are as follows:

$$(\mu_0^{\mathrm{ES}})^{\perp} = 2\pi N r_C^2 \lambda^2 \int_0^{2/\lambda} K^2 f_{\vec{S}}^2 (1 - e^{-2M_{\vec{S}}}) S\, dS\,, \tag{A1}$$

$$(\mu_H^{\mathrm{ES}})^{\perp} = N r_c^2 \lambda^2 \int_0^{2/\lambda} \int_0^{2\pi} K^2 f_{\vec{S}} f_{(\vec{S}-\vec{g})} \times [e^{-M_{\vec{g}}} - e^{-(M_{\vec{S}} + M_{(\vec{S}-\vec{g})})}]\, \dot{S}\, dS\, d\phi\,, \tag{A2}$$

where N is the number of atoms per cm^3, r_c is the classical radius of electron, λ is the wavelength of the x rays, $S = |\vec{S}| = 2\sin\theta/\lambda$, $g = |\vec{g}| = 1/d_{hkl}$ is the inverse of the spacing between the crystallographic planes $H \equiv h, k, l$, $f_{\vec{S}}$, $f_{(\vec{S}-\vec{g})}$ are the atomic scattering factors corresponding to the scattering vectors $\vec{S}$ and $\vec{S} - \vec{g}$, respectively, $M_{\vec{S}}$, $M_{\vec{g}}$, $M_{\vec{S}-\vec{g}}$ are the exponents of the Debye-Waller factor corresponding to the vectors $\vec{S}$, $\vec{g}$, and $\vec{S}-\vec{g}$, respectively, and $K=\cos\gamma$ is a polarization factor. γ is equal to the angle between the polarization vector of the radiation diffracted in anomalous transmission and the direction of the radiation scattered by the thermal vibrations. Formulas (A1) and (A2) are equal for $\vec{g}=0$.

The contribution μ_0^C of atom-pair correlations to the average absorption coefficient was calculated by using the following formula derived by Dederichs[27] for the Debye solid and for the perpendicularly polarized x-ray radiation:

$$(\mu_0^C)^{\perp}=2\pi(24\pi^2)^{2/3}Nr_c^2\hbar^2\lambda^2f^2e^{-2M}/kma^2d_{hkl}^2$$

$$\times\left\{\frac{1}{2\Theta}+\frac{T}{\Theta^2}\left[\ln\left(\frac{kT}{h\nu_c}(1-e^{-\Theta/T})\right)-\frac{3}{2}\right]\right\} \quad , \qquad \text{(A3)}$$

where $\hbar$ is the reduced Planck constant, k is the Boltzmann constant, m is the atom mass, a is the lattice parameter, Θ is the Debye temperature, and ν_c is the minimum frequency of the phonon in the crystal. ν_c was taken equal to $Vr_c\lambda fe^{-M}/\pi V_c\sin 2\theta$ (derived from the Darwin expression for the angular interval of total reflection), where V is the sound velocity and V_c is the volume of the unit cell. The other symbols of (A3) were previously defined.

Numerical calculations of the formulas (A1)–(A3) were performed by means of a computer in various cases; the results for room temperature are reported in Tables III and IV. An analytical expression of the atomic scattering factor f[28] with corrections for anomalous dispersion[29] was used for the computer program.

APPENDIX B: CONTRIBUTION OF BRAGG SCATTERING TO THE AVERAGE ABSORPTION COEFFICIENT

The experimental determination of the average absorption coefficient μ_0 is usually done by measuring the attenuation of a monochromatic x-ray beam through a polycrystalline sheet of the material. Then, the value of μ_0 contains the contribution of the scattering due to crystallites oriented for Bragg reflection by a set of crystallographic planes. Although this contribution is small, it is not negligible when the Debye temperature is determined from intensity measurements in anomalous transmission. The Bragg contribution to μ_0 can be estimated as follows. Suppose that the orientations of the crystallites in the sheet are completely random; that is, the aggregate does not have any preferred orientation. The percentage of crystallites for which the normal to the diffracting planes hkl lies in the interval θ and $\theta+d\theta$ is, then, given by $\frac{1}{2}\cos\theta\, d\theta$ and the integrated intensity R_{hkl} diffracted by the volume element dv of the aggregate is

$$R_{hkl}=\tfrac{1}{2}n\,dv\cos\theta\int I(\theta)\,d\theta \ ,$$

where n is the index of multiplicity of the planes hkl, $I(\theta)$ is the intensity diffracted at the glancing angle, and the integral is extended to the entire angular interval of the reflection. The expression of R_{hkl} can now be written in explicit form on the assumption that the crystallites diffract as mosaic crystals. It follows that the contribution μ_{BS} to the total absorption coefficient μ_0 is given by

$$\mu_{BS}=\tfrac{1}{2}(r_c\lambda N_0)^2\textstyle\sum_{hkl}K^2F_{hkl}^2nd_{hkl}e^{-2M} \ , \qquad \text{(B1)}$$

where N_0 is the number of unit cells per unit volume, K is the polarization factor equal to 1 and $\cos 2\theta$ for radiation with perpendicular and parallel polarization, respectively, F_{hkl} is the structure factor of planes $\{hkl\}$, and the other symbols were previously explained. The sum $\sum_{hkl}$ is extended to all possible reflections of the powder.

Formula (B1) was calculated by means of a computer for various temperatures, in the case of a polycrystalline sheet of Cu. The analytical expression and the anomalous dispersion corrections of the atomic scattering factor were the same as explained in Appendix A. As an example, the values of μ_{BS} for Cu $K\alpha$ radiation with perpendicular and parallel polarizations are, respectively, 14.38 and 4.64 cm^{-1} at 200 °K and decrease to 10.05 and 3.41 cm^{-1} for $T=900$ °K. In the experimental conditions used for the measurement of the linear absorption coefficient of Cu, $\mu_{BS}=9.54\ \text{cm}^{-1}$ at room temperature.

---

[1] C. Ghezzi, A. Merlini, S. Pace, and L. Ragnotti, Boll. Soc. Ital. Fis. 46, 18 (1965).

[2] T. O. Baldwin, Phys. Status Solidi 25, 71 (1968).

[3] T. O. Baldwin, F. W. Young, Jr., and A. Merlini, Phys. Rev. 163, 591 (1967).

[4] A. Merlini and S. Pace, Nuovo Cimento 35, 377 (1965).

[5] C. Ghezzi, A. Merlini, and S. Pace, Nuovo Cimento 49, 58 (1967).

[6] B. W. Batterman, Phys. Rev. 126, 1461 (1962).

[7] P. H. Dederichs, Physik Kondens. Materie 5, 347 (1966).

[8] A. A. Maradudin and P. A. Flinn, Phys. Rev. 129, 2529 (1963).

[9] A. Paskin, Acta Cryst. 10, 667 (1957).

[10] R. N. Kyutt and O. N. Efimov, Fiz. Tverd. Tela 11, 283, 1969 [Sov. Phys. Solid State 11, 228 (1969)].

[11] G. Hildebrandt and H. Wagenfeld, Acta Cryst. 16, A160 (1963).

[12] B. W. Batterman and D. R. Chipman, Phys. Rev. 127, 690 (1962).

[13] B. Okkerse, Philips Res. Rept. 17, 464 (1962).

[14] B. W. Batterman, Phys. Rev. 134, A1354 (1964).

[15] O. N. Efimov, Phys. Status Solidi 22, 297 (1967).

[16] J. Ludewig, Acta Cryst. A25, 116 (1969).

[17] By using $\mu_0 = 446\ \mathrm{cm}^{-1}$, as it was done in the work of Ref. 2, the Debye temperature of the present work should be increased by 2.5 °K.

[18] The correction of $\Theta = 306$ °K in Table VI was obtained by averaging the corrections due to phonon scattering and to the anharmonicity over the temperature range 77–377 °K.

[19] E. C. Svensson, B. N. Brockhouse, and J. M. Rowe, Phys. Rev. 155, 619 (1967).

[20] R. M. Nicklow, G. Gilat, H. G. Smith, L. J. Raubenheimer, and M. K. Wilkinson, Phys. Rev. 164, 922 (1967).

[21] This correction is in agreement with the difference between the Debye temperatures calculated from the vibrational spectra which were obtained at 49 and 298 °K by means of neutron-inelastic-scattering experiment (see Ref. 20). We are grateful to Dr. R. M. Nicklow for the communication of this result.

[22] D. R. Chipman and A. Paskin, J. Appl. Phys. 30, 1992 (1959).

[23] E. A. Owen and R. W. Williams, Proc. Roy. Soc. (London) A188, 509 (1947).

[24] P. A. Flinn, G. M. McManus, and J. A. Rayne, Phys. Rev. 123, 809 (1961).

[25] C. R. Hall and P. B. Hirsch, Proc. Roy. Soc. (London) A286, 158 (1965).

[26] Simple expressions of the formulas by Afanas'ev and Kagan are given in Ref. 15.

[27] Private communication. Formula (A3) is more general than that of Ref. 7, because it is valid even at low temperatures.

[28] D. T. Cromer and J. T. Waber, Acta Cryst. 18, 104 (1965).

[29] D. T. Cromer, Acta Cryst. 18, 17 (1965).