values by more than can be explained by the experimental error of the present measurements. In the previous work the value of $(c_{11}-c_{12})$ did not occur alone, as in the expression for $K[\bar{1}10]_{220}=2/(c_{11}-c_{12})$, but was involved in a more complex way with the elastic constants. The value of $K[\bar{1}10]_{220}$ is sensitive to a change in $(c_{11}-c_{12})$, and the slope of the corresponding line in Fig. 1 would have to be changed by an amount far outside the experimental error in order to bring the result into conformity with the value 0·74. One factor must not be overlooked and that is the possible failure of the diffuse reflexion theory owing to the large amplitude of thermal vibration of the lead atoms. However, the straight lines of Fig. 1 suggest that there is no breakdown of the theory as far as it applies to the first-order thermal scattering. Further, the photographic determination was carried out on points having no special relation to the rekha direction $[\bar{1}10]$ and the results are consistent with those obtained by the spectrometer study.

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An Apparent Anisotropic Debye–Waller Factor in Cubic Crystals

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Neutron and X-ray diffraction studies on α brass (70–30 f.c.c.) have revealed that the integrated intensities are reduced by a Debye–Waller temperature factor $\exp(-2B(\sin\theta/\lambda)^2)$, where B is not only a function of the characteristic temperature θ and the absolute temperature T, but also a function of crystal direction, contrary to present theories for cubic crystals. The effect is very marked in comparing the 222 and 400 peaks both as to their relative intensities and their change in intensity with temperature from liquid nitrogen to room temperatures.

In the course of neutron diffraction studies of cold-worked brass (f.c.c.) (Weiss, Clark, Corliss & Hastings, 1952) it was found that the relative intensities of the 200 to the 111 peaks in cold-worked as well as annealed brass was 6% smaller than calculated. The intensities of neutron powder diffraction peaks in transmission for a f.c.c. lattice are given by

$$I \propto J_{hkl} \exp[-\mu h \sec\theta] \exp[-2B(\sin\theta/\lambda)^2]/\sin^2 2\theta\ ,$$

where J_{hkl} is the multiplicity, $\exp[-uh\sec\theta]$ is the absorption factor and $\exp[-2B(\sin\theta/\lambda)^2]$ is the Debye–Waller temperature factor. Except for the Debye–Waller factor, all factors in the intensity expression are accurately defined. Extinction effects are negligible in neutron diffraction powder patterns for the 1 Å neutrons used in these measurements. The volume of the sample irradiated was approximately 60 cm.^{3} of 325 mesh powder, which makes preferred orientation effects negligible. The absorption factor is directly determined by transmission of the incident beam. The ratio of the absorption factor between the 111 peak, $2\theta = 30{\cdot}4°$ and the 200 peak $2\theta = 35{\cdot}2°$ is considered accurate to 0·1%. After applying a characteristic temperature of 310° K. (expected from elastic constants) in the Debye–Waller factor the ratio of the 200 to the 111 peaks was too low by $6\pm\frac{1}{2}$%. By artificially invoking a characteristic temperature of 215° K. to the 200 peak (the 111 peak remaining 310° K.) agreement was obtained. Neutron measurements on copper and nickel revealed the effect to be only about $2\pm\frac{1}{2}$%.

The measurements were continued with X-rays where attention was directed to the 222 and 400 peaks to enhance the Debye–Waller factor. In addition, measurements were made at both room temperature and at liquid-nitrogen temperatures. 325 mesh brass was poured into a sample holder and bound with collodion. Zirconium-filtered Mo $K\alpha$ radiation was used. Fig. 1 shows the experimental curves, each of which is a composite of about ten separate runs. The results are tabulated in Table 1. The characteristic temperatures of the 222 and 400 peaks were adjusted to fit the ratio of the observed integrated intensities for each reflection at room temperature and liquid-nitrogen temperature, and yielded $\theta = 380°$ K. for the 222 and $\theta = 215°$ K. for the 400 peaks. The room-temperature ratio of the 222 to the 400 peaks was also consistent to within 5% of this assignment in characteristic temperatures and deviated as much as 40% for calculations based on a $\theta = 310°$ K. for both peaks. Effects of preferred orientation would affect the relative observed intensities of the 222 to the 400 peaks but would cancel out in observations of each peak at different temperatures. Furthermore, less than 5% variation in relative intensities at room temperature was found amongst several samples and it is estimated that preferred-orientation effects would account for no more than 5%. Scattering factors were computed from Hartree–Fock wave functions for free atom Cu$^+$. Extinction was also estimated to be negligible for these peaks (Weiss, 1952; Long, 1953).

Table 1

Mo $K\alpha$ radiation (λ = 0·709 Å)

Ratio	Calculated ratio	Observed ratio
$\frac{(400)\ \text{L.N.}}{(400)\ \text{R.T.}}$	1·23 (θ = 310° K.) 1·58 (θ = 215° K.)	1·58
$\frac{(222)\ \text{L.N.}}{(222)\ \text{R.T.}}$	1·17 (θ = 310° K.) 1·13 (θ = 380° K.)	1·13
$\frac{(222)\ \text{R.T.}}{(400)\ \text{R.T.}}$	4·00 (θ_{222} = 380° K.; θ_{400} = 215° K.) 2·61 (θ_{222} = 310° K.; θ_{400} = 310° K.)	4·15

R.T.: Room temperature (295° K.).
L.N.: Liquid-nitrogen temperature (80° K.).

Finally, the room-temperature measurements were repeated with Ni $K\alpha$ (λ = 1·66 Å) on both brass and copper; the results are tabulated in Table 2. At this wavelength a θ of 250° K. for the 400 and a θ of 310° K. for the 222 was consistent with the data, whereas a θ of 310° K. for both peaks deviated by 17%. However, a θ of 320° K. for both peaks in copper (from specific heat) was consistent with the observations to within 5%.

While no satisfactory explanation is available to account for these results, the following theoretical

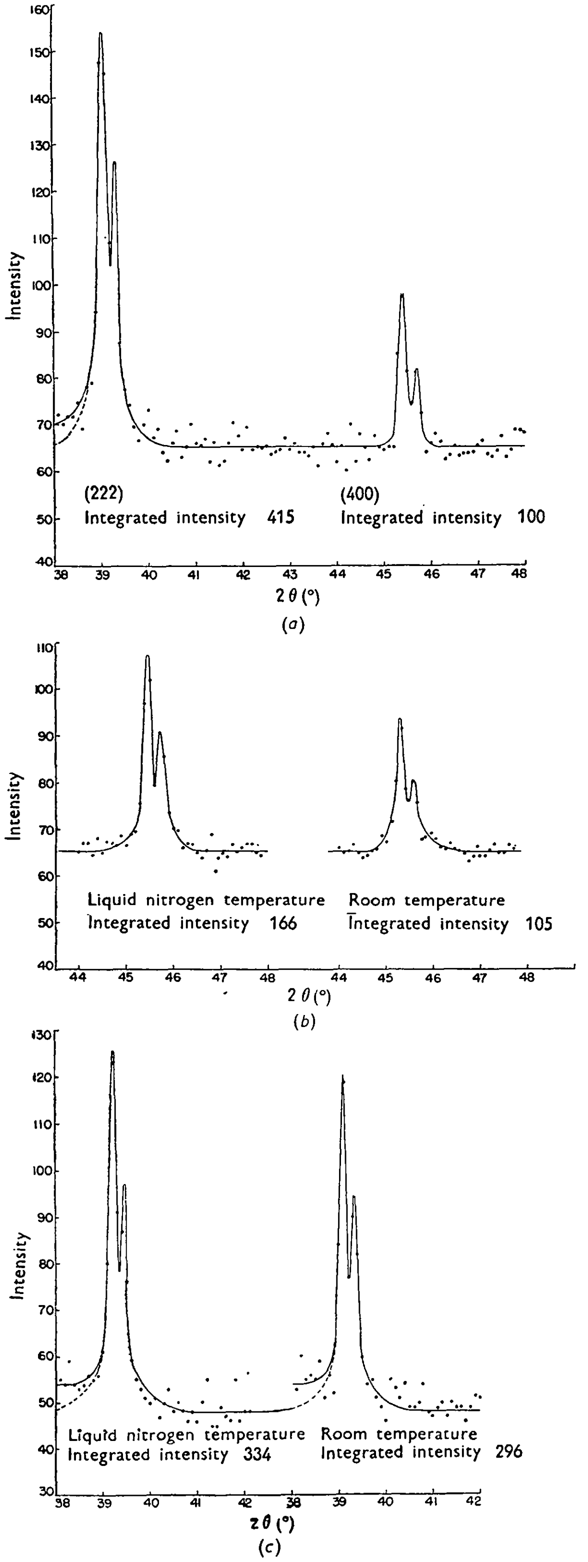

Fig. 1. (a) Relative intensities of 222 and 400 annealed α-brass peaks with Mo $K\alpha$ radiation.

(b) 400 annealed α-brass peaks at room and liquid-nitrogen temperatures with Mo $K\alpha$ radiation.

(c) 222 annealed α-brass peaks at room and liquid nitrogen temperatures with Mo $K\alpha$ radiation.

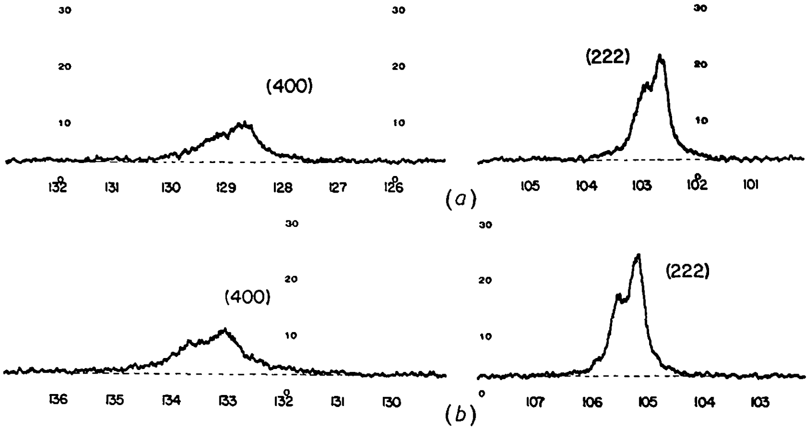

Fig. 2. (*a*) Diffraction pattern of 222 and 400 peaks of α-brass with Ni $K\alpha$ radiation.
(*b*) Diffraction pattern of 222 and 400 peaks of copper with Ni $K\alpha$ radiation.

Table 2

Ni $K\alpha$ radiation (λ = 1·66 Å)

Ratio	Calculated ratio	Observed ratio
$\frac{(222)\text{ R.T.}}{(400)\text{ R.T.}}$ (brass)	1·37 (θ_{222} = 310° K.; θ_{400} = 310° K.) 1·61 (θ_{222} = 310° K.; θ_{400} = 250° K.)	1·61
$\frac{(222)\text{ R.T.}}{(400)\text{ R.T.}}$ (copper)	1·21 (θ_{222} = 320° K.; θ_{400} = 320° K.)	1·28

R.T.: Room temperature (295° K.).

points should be emphasized. The independence on crystallographic direction of the factor B in the exponent of the Debye–Waller expression has been shown by Ott (1935), and merely depends on the validity of the harmonic-oscillator model for vibrations in the solid. This independence on crystallographic direction is also valid to the first order in the displacement vector (independent of the harmonic-oscillator assumption) if the displacements follow a gaussian distribution. Since one would hesitate to abandon both these assumptions, one must look elsewhere for an explanation.

Recently Warren (1953) has shown theoretically that the diffuse scattering in powders deviates appreciably from the independent-oscillator assumption which yields an angular dependence for the diffuse scattering equal to

$$I_{\text{diffuse}} \propto \{1-\exp[-2B(\sin\theta/\lambda)^2]\}\,.$$

Warren shows theoretically that the diffuse scattering in powders has maxima in the Bragg directions and it is therefore impossible to separate the elastic scattered radiation from the inelastic. Indeed, it was found that the patterns of annealed brass and copper with Ni $K\alpha$ radiation showed a continual decrease in background between the 222 and 400 peaks and reached a minimum midway between the two. These peaks are separated by about 30° in 2θ. The background, however, was arbitrarily drawn at a point which from visual inspection one might ordinarily take to be the background. This is shown in Fig. 2. Applying Warren's expressions as a correction to the observed intensities proved unsuccessful in explaining all of the above results, even though the inelastic contribution to the Bragg peaks is not negligible for powders.

From the data in Table 1, the calculated ratio of the 222/400 peaks in brass at liquid-nitrogen temperature is 2·49 while the observed ratio is 2·97, in much closer agreement than at room temperature. It therefore appears that until a satisfactory explanation is available, assurance of the Debye–Waller corrections for intensity can only be obtained from a temperature- and wavelength-dependent study of the intensities.

It is intended to repeat these measurements on single crystals, in which case separation of thermal diffuse scattering from Bragg intensities is more reliable.

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