& Rundle is three times the calculated standard deviation for the difference (0·008 Å) and thus would be significant. Other accurate data for the SO_4 ion are those of Singer & Cromer (1959) for zirconium sulphate; they found two significantly different S–O distances of 1·443 and 1·486 Å. It is possible that the calculated standard deviations are too low so that the above differences are not significant. It is also possible that one has to abandon the idea of the SO_4 ion being a regular tetrahedron of constant dimensions under all circumstances. More work on the SO_4 ion is needed to settle this question.

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Search for an Anisotropic Debye-Waller Factor in Cubic Copper-Base Solid Solutions

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A re-examination has been made of the Debye–Waller temperature factor $\exp\{-2B(\sin\theta/\lambda)^2\}$, where B, according to Weiss and co-workers, is a varying function of $\{hkl\}$ when measurements are made on α brass powder. The integrated and peak intensities of several different lines from powder samples of α brass and α aluminium bronze were obtained at 77 °K. and room temperature, with Mo $K\alpha$ radiation, after heat treatments designed to induce varying amounts of short-range order. It was found that deviations of B from isotropy were marginal and not significant except possibly for the 222 lines. No deviations comparable in magnitude with those reported by Weiss and co-workers were found.

Weiss and co-workers (1956) reported measurements of integrated intensities of the 222 and 400 Mo $K\alpha$ lines diffracted by α brass powder at 77 and 295 °K., and showed that these intensities could not be reconciled with the conventional expression $\exp\{-2B(\sin\theta/\lambda)^2\}$ for the Debye–Waller attenuation factor associated with thermal vibrations (hereafter abbreviated DWF), unless B was taken to be a function of direction in the crystal, so that for a given temperature B was different for 222 and 400. They reached this conclusion both by comparing intensities of the same line at two temperatures, and also by comparing intensities of the two lines at one temperature (and comparing these ratios with computed ratios obtained for various assumed values of B). Values of B were expressed in terms of the Debye characteristic temperature Θ, which accordingly turns out to be effectively a function of crystal direction (we refer to this as an 'anisotropy of the Debye temperature'); values of Θ so obtained do not agree with those calculated from calorimetric measurements on α brass.

Weiss and co-workers believed that the anisotropy of Θ discovered by them was inconsistent with the accepted quantum-mechanical model for thermal vibration and the DWF, which Ott (1935) had shown to imply isotropy of B, and therefore of Θ. Lonsdale & Grenville-Wells (1956) however pointed out that this apparent contradiction can be resolved if two different kinds of atom are present in the structure, since these can have two different amplitudes of vibration. They presented calculations for an imaginary binary compound and showed that a large anisotropy of B could easily result. The two atomic species must be ordered—i.e. occupy distinct sublattices—if B is to be anisotropic; if atoms are randomly distributed, as in a disordered solid solution, then their explanation is invalid (Lonsdale, 1958).

There is ample experimental evidence for anisotropic Debye–Waller factors resulting from unequal vibrations of two atomic species in ordered compounds. Good instances are the work by Chipman (1956) on partially ordered Cu_3Au, and by Jack & Wachtel (1957) on the partially ordered compound Cs_3Sb.

The presence of some kind of crystallographic order in α brass must thus be presumed to explain the results of Weiss and co-workers; if it exists at all, this order (which has never been directly verified) must be a form of *short-range* order (Clarebrough *et al.*, 1960) and it is surprising that so incomplete a form of order should result in a substantial anisotropy in the DWF. (Recent calculations by Krivoglaz (1959) imply that the creation of short-range order, by reducing lattice distortions, might indeed reduce anisotropy of the DWF.) If, however, short range order *does* have this effect, then measurements of the anisotropy of the DWF would provide a valuable indirect means of testing for the presence of short-range orders in alloys such as brass where the direct X-ray method cannot be applied. Experiments have accordingly been carried out to check Weiss' results and also to make similar measurements on α aluminium bronze (copper-rich Cu/Al alloy) which is known, from measurements of diffuse scattering of X-rays, to possess short-range order (Houska & Averbach, 1959; Kagan *et al.*, 1960; Davies & Cahn, 1962). By varying the heat treatment of α aluminium bronze, the degree of short-range order can be varied (Davies & Cahn, 1962), and this should affect the amount of anisotropy, if any, of the DWF. This point was investigated for α aluminium bronze and also for α brass, which can also be ordered by heat treatment (Clarebrough *et al.*, 1960).

Experimental methods

Diffractometer briquettes made from filings were compacted *in situ* in a low-temperature attachment for a Philips diffractometer (Butters & Myers, 1955). This allowed the samples to be held stably for long periods at the temperature, 77 °K., of boiling liquid nitrogen; the sample temperature was continuously recorded. Filtered Mo $K\alpha$ radiation was used and diffracted intensities were measured by means of a scintillation counter provided with pulse-height analysis, a combination which reduced the background level and prevented errors due to counting loss at high counting rates. Line profiles were determined to a fixed statistical accuracy and plotted automatically by means of a counting-rate computer (Hamacher & Lowitzsch, 1956). The complete circuit, including the X-ray source, was subjected to frequent checks of stability and linearity.

In view of Chipman & Paskin's (1959) demonstration that the long tails of diffraction lines are actually due to thermal diffuse scattering, these tails were not included in the measurements of integrated intensity. Peak heights of the smoothed profiles, which should be accurately proportional to integrated intensities for a given line at two temperatures, were also recorded. In repeat runs, integrated intensities showed rather more scatter than did peak heights, possibly because of small fluctuations in sample temperature (Haworth, 1960); both measures of intensity are therefore recorded in the tables. The observed intensity ratios for each line have been corrected for changes of the Lorentz-polarization factor and of f with Bragg angle and therefore with temperature; the total correction was of the order of 1·5%. The further correction for change of Θ with lattice parameter (and therefore with temperature) was sufficiently small, over the temperature range concerned, to be neglected.

The heat treatments intended to produce enhanced short-range order in the alloys were selected by reference to an X-ray scattering study on aluminium bronze (Davies & Cahn, 1962) and to lattice-parameter measurements on brass (Feder *et al.*, 1958). Details are given in Tables 2–4.

Table 1. *Thermal (intensity) ratios* ($TR = I_{77\,°K.}/I_{300\,°K.}$) *for pure precipitated copper*

Line	Integr. intens. (obs., corr.)	Peak heights (obs., corr.)	Integr. intens. (calc. for $\Theta = 320$ °K.)	Approx. $\Delta\Theta$ corresp. to change of $+0{\cdot}01$ in TR (°K.)
222	0·85	$0{\cdot}85_5$	0·84	14
331	0·75	0·75	$0{\cdot}76_5$	10
420	$0{\cdot}76_5$	$0{\cdot}77_5$	0·76	10
531	$0{\cdot}64_5$	$0{\cdot}62_5$	0·61	5
600, 442	0·64	$0{\cdot}61_5$	$0{\cdot}60_5$	5

The apparatus was tested by making measurements on pure chemically precipitated copper powder of very fine particle size, with results shown in Table 1. The thermal ratios (TR = intensity of line at 77 °K./intensity of same line at 300 °K.) were in agreement with TR calculated from the calorimetric value of Θ (appropriately corrected for the conditions of the experiment, following the arguments of Blackman, 1955), i.e. 320 ± 5 °K., within the experimental error of $\sim 2\%$. No lines at lower Bragg angles than 222

Table 2. *Thermal ratios for* 70/30 *brass filings*

(*a*) Quenched from 450 °C. (*b*) Quenched from 650 °C. (*c*) Quenched from 450 °C. and annealed 132 hr. at 150 °C. (*d*) Quenched from 450 °C. and annealed 750 hr. at 135 °C.

	Integrated intensities (obs., corr.)				Peak heights (obs., corr.)							
Line	(*a*)	(*b*)	(*c*)	(*d*)	(*a*)	(*b*)	(*c*)	(*d*)	Mean of preceding 8 cols.	Integr. intens. calc. for $\Theta = 295$ °K.	*TR* reported by Weiss *et al.*	Approx. $\Delta\Theta$ corresp. to change of +0·01 in *TR* (°K.)
222	0·82	0·88	$0{\cdot}81_5$	$0{\cdot}83_5$	$0{\cdot}84_5$	$0{\cdot}91_5$	$0{\cdot}85_5$	$0{\cdot}81_5$	0·85	$0{\cdot}82_5$	0·88*	14
400	$0{\cdot}77_5$	0·75	$0{\cdot}82_5$	0·74	$0{\cdot}81_5$	0·79	0·83	0·77	$0{\cdot}78_5$	0·79	$0{\cdot}63_5$†	12
420	—	0·75	—	—	—	0·78	—	—	$0{\cdot}76_5$	$0{\cdot}74_5$	—	10
422	—	$0{\cdot}67_5$	0·74	0·71	—	$0{\cdot}73_5$	0·75	0·70	0·72	0·71	—	9
511, 333	—	$0{\cdot}72_5$	—	—	—	$0{\cdot}74_5$	—	—	$0{\cdot}73_5$	0·68	—	8
531	$0{\cdot}59_5$	$0{\cdot}61_5$	—	$0{\cdot}59_5$	0·60	$0{\cdot}66_5$	—	0·62	$0{\cdot}61_5$	$0{\cdot}59_5$	—	5
600, 442	0·55	—	—	—	$0{\cdot}58_5$	—	—	—	0·57	0·59	—	5

* Weiss' estimate for Θ from (222) = 380 °K. † Weiss' estimate for Θ from (400) = 215° K.

were measured; their intensities are too insensitive to changes in Θ. Unfortunately, the experimental accuracy in *TR* was somewhat less for the alloy samples because of their relatively coarse grain size. This results in unfavourable 'particle statistics' (de Wolff *et al.*, 1959) which cannot be eliminated by prolonged counting. The error from this source is normally reduced by spinning the sample in its own plane, but this could not be done at 77 °K.; an attempt to reduce the error by imparting small angular oscillations to the sample (Berthold, 1955) was unsuccessful. The error was minimized by sieving the powders through micro-sieves with 30μ holes (made by Buckbee Mears Inc., St. Paul, Minnesota) and by duplicating several runs with fresh samples.

No attempt was made to draw any conclusions from relative intensities of different lines at the same temperature, as had been done by Weiss and coworkers, because such ratios are too much subject to both random and systematic errors—especially extinction (Batsur' *et al.*, 1959) and absorption errors arising from air gaps between powder particles (Wilchinsky, 1951; de Wolff, 1956). For pure copper, for instance, the ratio I_{400}/I_{222} (which Weiss had used) at room temperature was 10–20% lower than the theoretical ratio. In fact this particular ratio seemed subject to an especially large error. A further complication arises from the presence of so-called 'static displacements' of atoms (Houska & Averbach, 1959), which should, however, have negligible effect upon the *TR*.

Table 3. *Thermal ratios for* Cu/Al *alloy with* 14·5 at.% Al

(*a*) Quenched from 450 °C., (*b*) quenched from 450 °C. and annealed 130 hr. at 150 °C.

	Peak heights (obs., corr.)			
Line	(*a*)	(*b*)	Integr. intens. (calc. for Cu)*	Integr. intens. (calc. for 70/30 brass)*
222	$0{\cdot}86_5$	$0{\cdot}85_5$	0·84	$0{\cdot}82_5$
400	0·80	—	$0{\cdot}80_5$	0·79
420	—	0·74	0·76	$0{\cdot}74_5$
531	0·62	0·60	0·61	$0{\cdot}59_5$
600, 442	0·59	—	0·61	$0{\cdot}59_5$

* The correct theoretical value of *TR* for this alloy (Θ unknown) is expected to lie between the values of the last two columns.

Table 2 lists results obtained with 70/30 brass in four different states of heat treatment. This table also includes a column in which is listed the approximate change in the derived value of Debye temperature corresponding to a change of thermal ratio by +0·01; this column applies equally to figures in Tables 3 and 4, which record results for aluminium bronze

Table 4. *Thermal ratios for* Cu/Al *alloy with* 15 at.% Al

(*a*) Quenched from 450 °C. (*b*) Quenched from 450 °C. and annealed 500 hr. at 165 °C.

	Integr. intens. (obs., corr.)		Peak heights (obs., corr.)				
Line	(*a*)	(*b*)	(*a*)	(*b*)	Mean of preceding 4 columns	Integr. intens. (calc. for Cu)*	Integr. intens. (calc. for 70/30 brass)*
222	0·89	0·81	$0{\cdot}87_5$	0·85	$0{\cdot}85_5$	0·84	$0{\cdot}82_5$
400	0·79	—	$0{\cdot}77_5$	—	$0{\cdot}78_5$	$0{\cdot}80_5$	0·79
420	—	0·73	—	0·73	0·73	0·76	$0{\cdot}74_5$
422	0·75	0·76	$0{\cdot}75_5$	$0{\cdot}73_5$	0·75	$0{\cdot}72_5$	0·71
511, 333	—	$0{\cdot}75_5$	0·75	0·75	0·75	$0{\cdot}69_5$	0·68
531	—	0·65	—	0·63	0·64	$0{\cdot}60_5$	$0{\cdot}58_5$

* The correct theoretical value of *TR* for this alloy (Θ unknown) is expected to be between the values of the last two columns.

from two different sources. The calorimetric value of Θ for brass (Table 2) is taken from Rayne (1957), and has again been corrected to match the temperatures used in the X-ray experiment.

Conclusions

The conclusions to be drawn from Tables 2–4 are:

(1) The only indication of anisotropy of the DWF is the consistently high level of the observed *TR* for 222. The discrepancy with theory is about the same for both alloys. The few measurements of 511, 333 also gave high *TR* values, which is to be expected if the anomaly for 222 is genuine, since 222 and 333 are orders from the same family of diffracting planes. Nevertheless, the disparity of DWF for 222 is so small that its significance must be regarded as marginal. The discrepancy between mean observed and calculated *TR* for 222 is only half as large as that reported by Weiss and co-workers (Table 2).

(2) No significant discrepancy between mean measured and computed *TR* was found in either alloy for 400, whereas Weiss and co-workers had reported a very large discrepancy for 400 from brass (Table 2). Other diffracted lines again showed no significant anomalies in *TR* (with the possible exception of 422 and 531 in Table 4).

(3) No systematic changes in any *TR* were produced by heat treatment of either alloy, *i. e.* no correlation could be confirmed between *TR* and short-range order. In particular, *TR* for 222 was not systematically affected by heat treatment, and therefore short-range order does not accentuate the anisotropy of the DWF.

Any effective 'anisotropy of Θ' is therefore much smaller than the results of Weiss and co-workers would indicate, and it is not certain that it exists at all. The slightly high values of the 222 *TR*'s could conceivably be associated with extinction, which is itself a function of integrated intensity and would thus tend to increase the *TR* slightly (since extinction would be proportionately greater at the lower temperature).

The only way to achieve certainty concerning the perfect isotropy of the DWF for random or short-range ordered cubic alloys will be to make precision measurements of integrated intensities from single crystals, using the techniques employed by Chipman (1956) for Cu_3Au with long range order.

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