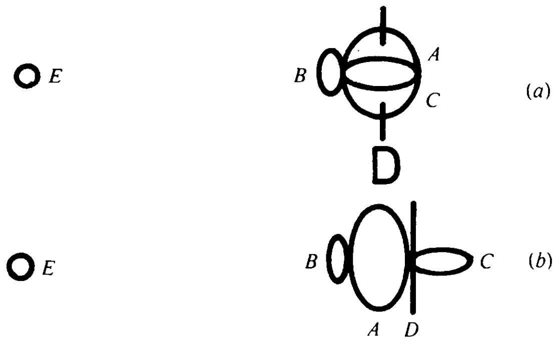

Fig. 2. Schematic illustration of the patterns in Fig. 1. (*a*) and (*b*) correspond to Fig. 1(*a*) and (*b*).

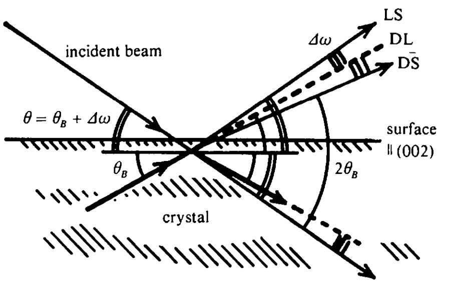

Fig. 3. Propagation direction of the radiation in the present X-ray diffraction experiment.

nearly equal to the deviation angle $\Delta\omega$ of the glancing angle from the Bragg angle θ_B.

The origin of the defect line is explained as follows. Fig. 3 illustrates schematically the propagation of the X-rays in real space. We consider the Bragg case in which the surface of the crystal is parallel to the reflecting net planes in the crystal. The deviation angle $\Delta\omega$ of the glancing angle of the incident beam from the 002 Bragg angle is less than a few degrees. A Laue spot (LS) is caused in the direction with scattering angle $2\theta_B + 2\Delta\omega$ by the mirror reflection of the incident white radiation. Intensity maximum of a diffuse spot (DS) due to the TDS is observed in the direction with scattering angle close to $2\theta_B$. If a cone of the TDS is incident on the 002 reflection planes with the Bragg angle θ_B in the crystal, the direction of the TDS is changed by the 002 reflection in the crystal. Thus the defect line (DL) is caused in the diffuse spot. It will be easily understood from Fig. 3 that the defect white line is observed in the middle between the Laue spot and the diffuse spot.

We therefore conclude that the defect line, *i.e.* the diffraction pattern caused by the Bragg reflection of TDS, was observed in the 002 diffuse spot from the pyrolytic graphite crystal.

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On some X-ray diffuse scattering effects on Cu–Al single crystals.

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Abstract

A change in the diffuse scattering intensity distribution as a function of Al concentration in the α-phase Cu–Al solid solution is examined. The shape and intensity of the diffuse $\bar{1}11$ and 020 reflexions are shown to change with increasing Al concentration. With 10 at.% Al as the starting point, new diffuse reflexions appear. These are interpreted in terms of the formation of new Al atom configurations.

Recently, the Cu–Al system has been the subject of a number of detailed studies, and so far the structure type occurring in the α-phase solid solution of this compound has not been elucidated. Measurement of diffuse scattering shows that with ~11 at.% Al as the starting point, these alloys reveal short-range order (Iveronova & Katsnelson, 1977). At lower Al concentrations the diffuse scattering is weak, and quantitative results on the structures are not reliable (Epperson, Fürnrohr & Ortiz, 1978). Analysis of the diffuse scattering distribution, however, gives qualitative evidence for the variations in the state of the alloying component at concentrations less than 10 at.% Al. The X-ray patterns correlate with the behaviour of the mechanical characteristics of the alloy (Braude, Gluzman, Demirsky & Komnic, 1981).

Experimental

Studies were carried out on single crystals of Cu and its alloys. Initial materials were of 99·996% Cu and 99·999% Al purity. The samples were annealed at ~1273 K for 8 h in

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an Ar atmosphere. The sample surface was close to (111) (to within 4°) and the sample axis to [$\bar{3}21$]. The samples were electrolytically thinned to 0·02–0·05 mm.

The diffuse scattering was measured with monochromated Cu $K\alpha$ radiation. Exposure varied from 40 to 90 h depending on the resulting sample thickness. The intensity was recorded on RT-1 film and measured with an IFO-451 densitometer. Optical-density diagrams were plotted (Wooster, 1963).

Results and discussion

Pure copper and Cu–Al alloys show four diffuse reflexions, at the reciprocal-lattice sites of type 200 (reflexion 1) and type 111 (reflexions 2, 3, 4) (Fig. 1). To study the intensity distribution and spot shapes, two sites were chosen: 020 and one of the $\bar{1}11$ sites (No. 2).

The diffuse scattering intensity distribution for Cu containing 0, 3, 5, 10, and 14 at.% Al is shown in Fig. 2(*a*)–(*g*), respectively. It is seen that for pure copper site $\bar{1}11$ has a slightly ellipsoidal shape, while site 020 is extended along [110] and [$\bar{1}10$] (Fig. 2*a*). These shapes may be attributed to the elastic anisotropy of Cu. Our calculation of the site 111 and 020 shapes from the absolute values of the elastic constants using Jahn's formula (Wooster, 1963) proved that our assumption was valid. The reflexions in question differ not only in shape but also in intensity. The maximum intensity measured from isointensity curves appeared to be 150 per unit value for reflexion $\bar{1}11$ and 50 per unit value for reflexion 020. The maximum intensity and diffuse spot for Cu–3 at.% Al are similar to those for pure copper (Fig. 2*b*).

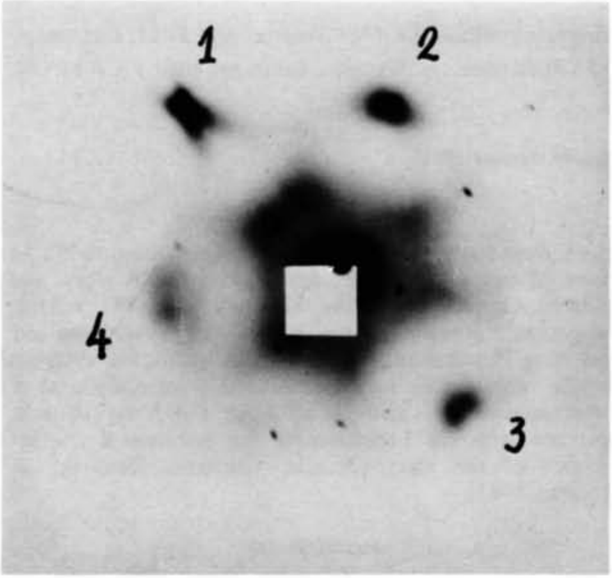

Fig. 1. X-ray picture of diffuse scattering of a Cu–10 at.% Al single crystal taken from the (111) plane. (Reflexions 1, 2, 3, 4 correspond to sites 020, $\bar{1}11$, $1\bar{1}1$, $\bar{1}1\bar{1}$, respectively.)

X-ray pictures of Cu–5 at.% Al crystals (Fig. 2*c*) permitted a number of new specific features in the isointensity curves to be revealed. Both reflexions have elongations of weak intensity along ⟨211⟩-type directions. These elongations occupy an appreciable part of the diffuse spot.

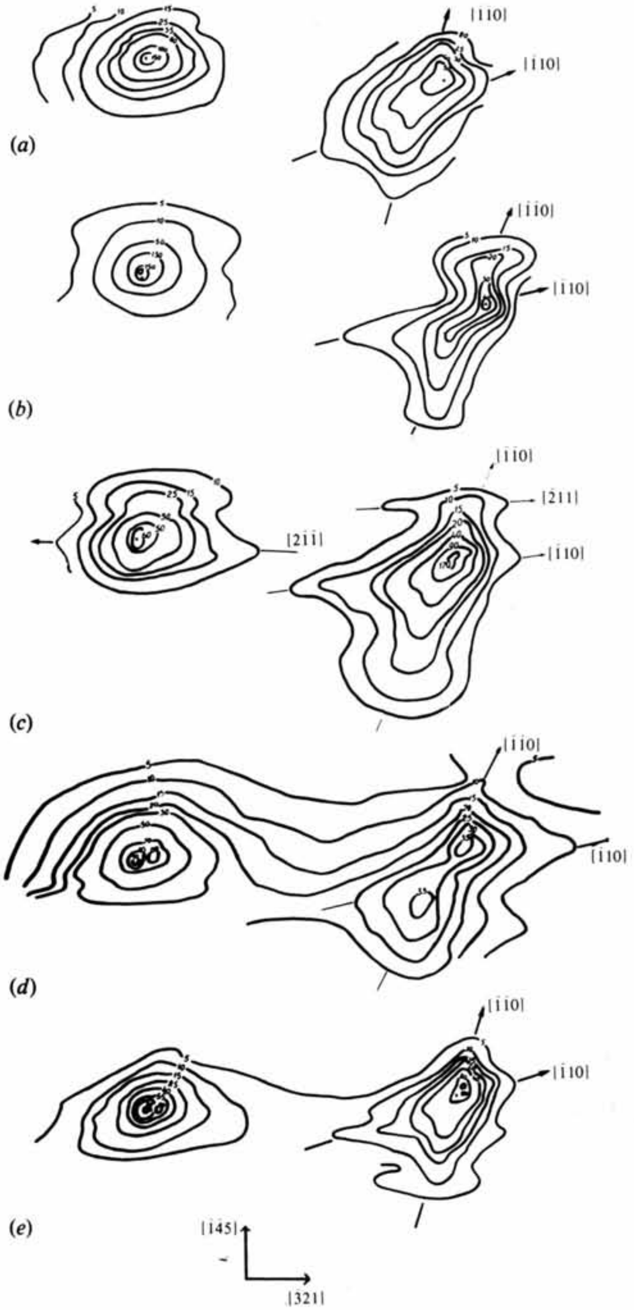

Fig. 2. Isointensity contour diagrams in the (111) plane near sites $\bar{1}11$ and 020 for α-phase Cu–Al solid solutions: (*a*) 0; (*b*) 3; (*c*) 5; (*d*) 10; (*e*) 14 at.% Al. Contour levels (per unit value): (*a*) 5–150 for $\bar{1}11$ [20–50 for 020]; (*b*) 5–150 [5–40]; (*c*) 5–60 [5–170]; (*d*) 5–90 [5–35]; (*e*) 5–80 [5–110].

It may be assumed that the elongations observed correspond to plate formation in the solid-solution matrix, in which case we estimate these regions to be about 40 Å across and four atomic layers thick.

The structural changes in the Cu–5 at.% Al crystal are shown by the way in which the intensities are redistributed: the maximum intensity in the central part of the 020 reflexion increases to 120 per unit value and that of $\bar{1}11$ decreases to 60 per unit value. The intensity change may be attributed to the formation of Al atom clusters which distort the regularity of the matrix (Cu atoms are appreciably smaller than Al atoms). This causes distortions which, in their turn, change intensities.

A further increase in the alloying-element concentration leads to a change in the diffuse intensity distribution. The shapes of isointensity curves for Cu alloyed with 10 and 14 at.% Al are shown in Fig. 2(*d*) and (*e*) respectively. Between the $\bar{1}11$ and 020 sites there are elongations of weak intensity. Measurement between the $\bar{1}11$ and 020 sites as a function of scattering angle (or displacement vector **g**) shows that the intensity drops in proportion to $1/g$ (a log plot, Fig. 3), as expected for large distortions (Krivoglaz, 1967). It is therefore reasonable to expect that an increase in the alloying-element concentration would be accompanied by appreciable distortions in the solid-solution lattice.

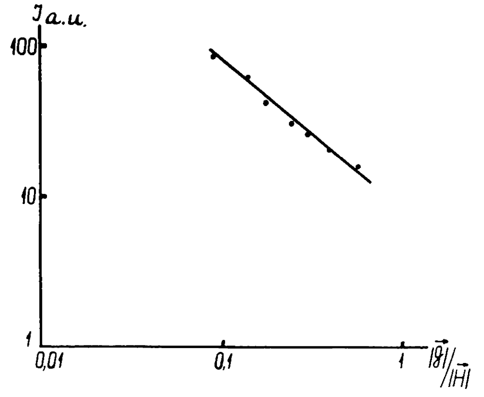

Fig. 3. Dependence of diffuse scattering intensity on displacement wavevector |**g**|.

These distortions might be associated with the formation of atom conglomerations within the solid-solution structure which lose coherence with the matrix lattice. This is supported by separation of sites $\bar{1}11$ and 020 (Fig. 2*d*,*e*).

In addition, the X-ray pictures of Cu–10 and 14 at.% Al display new diffuse reflexions which are absent at lower Al concentrations. As seen in Fig. 1, the six diffuse reflexions observed are near the primary beam at the vertices of a perfect hexagon whose sides are formed by the diffuse background in the shape of hyperbolae pointing towards the primary beam. The intensity of the six spots is roughly similar to that of the four diffuse reflexions considered earlier.

It is difficult to propose an unambiguous interpretation of the new diffuse reflexions. They may arise from the new configurations of Al atoms about Cu atoms. A configuration was considered (Epperson, Fürurohr & Ortiz, 1978) in which four Al atoms occupy a tetrahedron centred on the Cu atom with four Al atoms at the vertices. This corresponds to the trigonal symmetry of the six diffuse reflexions. It may be assumed that the new reflexions together with the $\bar{1}11$, 020 reflexions' separation indicate that the new regions appear. At growing concentrations these regions become nucleation centres for the new α_2 phase.

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Comments on *The rigid-body vibrations of molecules in crystals* by Burns, Ferrier & McMullan (1967).

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Abstract

The rigid-body analysis of the thermal vibrations in seventeen molecular structures by Burns, Ferrier & McMullan [*Acta Cryst.* (1967), **22**, 623–629] has been repeated and major discrepancies have been observed. The sources of errors have been diagnosed and the relevant comments together with the new list of results are reported.

The criterion put forward by Burns *et al.* (1967) (BFM1) for the verification of the assumed rigid-body motion of molecules has been used by various authors in their work

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