

R_e in four different hydrates and ice are all equal within the experimental uncertainty, $\pm 0.01 \text{ \AA}$, and equal to the corresponding distance in the free molecule, should therefore not necessarily mean that the configuration of the H_2O molecule does not change appreciably in these compounds; it might be that the change is such as to lead to an insignificant change in R_e .

The observed angle between the c axis and R_e , φ_0 , is somewhat larger in RbOMH , 26° , than in KOMH , 22° . This is in accordance with the crystal structure where the angle between the c axis and the plane determined by the two hydrogen bond acceptors and the water molecule is also larger in RbOMH , 29.5° , than in KOMH , 27° . These results seem to indicate that the water molecule is twisted out of the plane determined by the hydrogen bond acceptors and the water molecule. This conclusion is supported both by the neutron diffraction study of KOMH by Chidambaram *et al.* (1964), where the same results are obtained, and the model proposed by McGrath & Paine (1964), where this twist is explained as being due to the proximity of the surrounding cations.

Conclusion

The equilibrium proton-proton distance in the water molecule has been found to be $1.5341 \pm 0.0030 \text{ \AA}$ in potassium oxalate monohydrate and $1.5474 \pm 0.0030 \text{ \AA}$ in the isomorphous rubidium oxalate monohydrate from an analysis of the room temperature proton magnetic-resonance spectra of the two salts. The effects of the motion of the water molecule have been corrected for on the basis of a method given by Pedersen (1964) and a model of the motion given by McGrath & Paine (1964). The difference between the two values of the equilibrium distance obtained in the two salts are concluded to be significant, and also significantly different from the value of the corresponding distance in the free molecule, 1.514 \AA . The stretching of R_e in

the two oxalates is explained on the basis of the known crystal structures, as determined by Pedersen (B.F., 1964, 1965), as resulting from effects of non-linear hydrogen bonds.

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The Structure of Liquid Aluminum-Iron Alloys

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X-ray diffraction measurements have been made on liquid alloys of aluminum containing up to 4 at. % of iron, at temperatures between 760°C and 1000°C . The results indicate that the liquids consist of a random array of the two types of atom and do not contain polyhedral structural units of the type found in the intermetallic compounds occurring in the solid phase of these alloys. This conclusion is supported by calculations of the scattering expected from various random and polyhedral models. A detailed fit of observed to calculated scattering cannot be made because of the difficulty of constructing accurate radial distribution functions for a multi-component system.

Introduction

The compounds which are found in aluminum-rich alloys of aluminum with transition metals are char-

acterized by very narrow ranges of composition and complicated crystal structures. According to one interpretation (Black, 1956) the significant features of these structures are the polyhedra formed by the arrangements of aluminum atoms around a central transition

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metal atom. The polyhedra contain between eight and twelve aluminum atoms, and the long range complexity of many of the structures is explained by the difficulty of linking together nine- and ten-point polyhedra in a continuous three-dimensional array. The contraction of the mean aluminum to transition atom distance within the polyhedra and the fact that direct contact between transition metal atoms is usually avoided both suggest that the strongest bonds in these structures are those between unlike atoms within each polyhedron. An alternative, but not necessarily exclusive, interpretation is that the significant features of the structures are the extremely short distances which are found for a few of the transition metal to aluminum contacts. Brown (1959, 1962) has pointed out that the shortest distances always occur when one aluminum atom is bonded to only two transition metal atoms and that in these cases the three atoms lie in a straight line; this suggests that particular links are important for the stability of a structure rather than the polyhedral units as a whole.

If it is true that the bonds between a transition metal atom and the aluminum neighbours on the polyhedron surrounding it are the strongest bonds in a structure, then it might be expected that after melting the polyhedral units would still persist even although the regular linkages between polyhedra would have broken down. We have attempted to examine this possibility by X-ray diffraction studies of liquid alloys of aluminum with a small proportion (2-4 at.%) of iron. The solid solubility of iron in aluminum is very low (0.02% at 600°C) and at these compositions solid alloys consist of almost pure aluminum and crystals of $\text{Fe}_4\text{Al}_{13}$ (or the metastable FeAl_6). Hence it would be reasonable to assume that above the liquidus these alloys might consist of free liquid aluminum together with polyhedral units of the type found in $\text{Fe}_4\text{Al}_{13}$. Alternatively the liquid might consist of a random array of iron and aluminum atoms. X-ray diffraction data should indicate which of these models is correct.

Density measurements on liquid iron-aluminum alloys at these concentrations show that the mean interatomic distance between iron and aluminum must, as in the solid structures, be appreciably shorter than the sum of the normal atomic radii (Gebhardt, Becker & Dorner 1953). This is a feature which can be accommodated by either model.

Apparatus and measurements

The apparatus used has been described elsewhere (Cundall, 1963; Black & Cundall, 1965). Suitable quantities of alloy, prepared by melting aluminum-iron master alloys (kindly supplied by the British Aluminium Company, containing 41.3% Fe, 0.06% Cu, 0.06% Si and 0.35% Mn) with appropriate amounts of superpure aluminum (99.99% kindly supplied by Aluminium Laboratories Ltd) were melted in an alumina crucible under vacuum and held until the free horizontal sur-

face from which X-rays were scattered had lost all traces of oxide and gave good optical reflexion. The compositions of specimens and the possible variation of composition with height in the crucible were checked by chemical analyses of specimens after X-ray measurements on them had been completed. These measurements showed that errors introduced by assuming that the surface layers of liquid alloy had the same composition as the bulk solid before melting would be too small to affect the results significantly.

As in the previous work with this apparatus, evaporation of the liquid onto the windows of the vacuum furnace gradually reduced the intensity of the incident and scattered X-rays, and although it was possible to correct for systematic errors arising from this effect the gradual reduction did limit the duration of measurement runs. However, in the time available sufficient counts were usually recorded to make the random errors less serious than the systematic errors.

In order to compare the experimental curves with those calculated for the various models the measured intensities were first corrected for the effect of back-ground, polarization, absorption in the specimen and aberration from the ideal Bragg-Brentano focusing (Cundall, 1963; Black & Cundall 1965). The data were then placed on an absolute scale by fitting the high-angle regions of the curves to the curve of the sum of the mean square of the atomic scattering factors and the Compton scattering (modified by the monochromator efficiency) for the alloy concerned. The atomic scattering factors used, both for this purpose and for the calculations discussed below, were the curves of Freeman & Wood (1959) for iron and of Freeman (1959) for aluminum. We have discussed elsewhere (Black & Cundall, 1965) evidence that scaling factors obtained in this way may be subject to systematic error. This error does not seriously affect the conclusions which we draw from the data presented here, but it does mean that, when this and other sources of error are taken into account, the absolute scales of our various results are only reliable to within about 10%.

The experimental results are summarized in Table 1; in Fig. 1 a typical scattering curve for an alloy is compared with a curve for pure aluminum at the same temperature. In the table, each curve is described by parameters, corresponding to the labels of Fig. 1, which specify its main features. The full curves are available elsewhere (Cundall, 1963).

Methods of interpretation

Scattering measurements from a monatomic liquid can be used to derive, by the appropriate Fourier transform, either an electronic or an atomic radial distribution function (abbreviated below to r.d.f.) (James, 1948; Finbak, 1949). For a two-component liquid an electronic r.d.f. is the sum of the $A-A$, $A-B$ and $B-B$ functions, where A and B are the two components, whilst an atomic r.d.f. is the sum of convolutions of

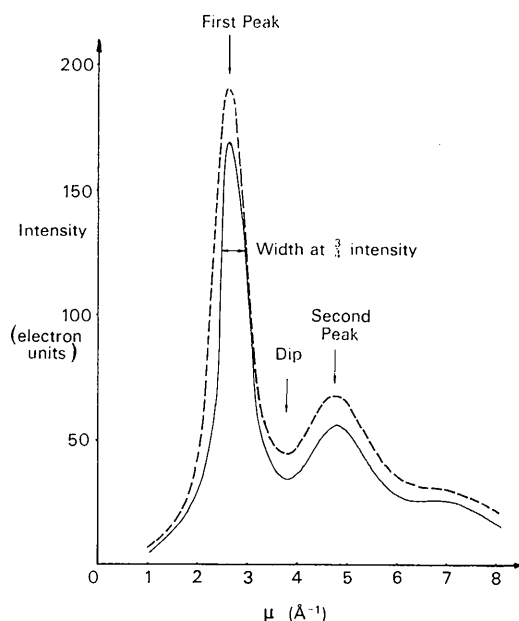


Fig. 1. Typical experimental intensity curves for pure aluminum and for alloy. Full line: aluminum at 800°C; dashed line: alloy containing 1.8 at. %Fe at 800°C. Labels correspond to those used in Tables 1 and 2.

each of the three atomic r.d.f.'s (Waser & Schomaker, 1953). In both cases there is no unambiguous way of separating the result into the three component functions, although in special cases the transforms might show special features which can be interpreted (see *e.g.* Levy, Agron & Danford, 1959).

Many workers have used approximate methods for interpreting the particular systems they were considering. For example, Smallman & Frost (1956) and Krebs, Haucke & Wegard (1958) investigated alloys of elements which were adjacent in the periodic table, so that they could assume that the scattering factors and r.d.f.'s of the components were very similar. Warren, Krutter & Morningstar (1936) showed that the analysis of the atomic r.d.f. is simplified if it can be assumed that the scattering factors of the different atoms are identical except for a single scaling factor. This method has been applied to liquid alloys by Gingrich & Henderson (1952) and Orton, Shaw & Williams (1960). For

iron and aluminum, the ratio of the scattering factors varies from 2.0 in the forward direction to 2.9 at $\sin \theta/\lambda = 1.1$ (where λ is the radiation wavelength), so that this method is not suitable. Finally, some workers, *e.g.* Hendus (1947) in his work on gold-tin alloys, have given a qualitative interpretation of their data comparing positions of peaks in the scattering with the positions expected from prominent interatomic distances in the solid alloys: this method has been criticized by Fournet (1957).

Electronic r.d.f.'s were obtained by Fourier transformation of some of the results obtained in the present work. They were appreciably affected by spurious ripples caused by termination effects and the effect of systematic errors in the scaling factor; although these ripples can be ignored by drawing a mean curve through them, the accuracy of this curve is not high and so this method of interpretation was abandoned.

It was apparent that none of the methods used by other workers would be suitable for analysis of these dilute iron-aluminum alloys, and a more direct method was adopted. The measured curves were compared directly with predicted curves for the scattered intensity which were computed on the basis of various model liquids. In this method, the effects of systematic errors due to the low and high angle limits on the experimental data, and the problems of unravelling the composite curves yielded by direct data transforms, are avoided. However, it is necessary to vary the parameters of any proposed structure to determine which of its features are demanded by the data and which can be varied, either individually or jointly, without significantly altering the agreement with experiment.

The model calculations

The intensity given by a model liquid is computed from the equation:

$$I(\mu) = \sum_p \sum_q f_p f_q \exp[-ikS \cdot (\mathbf{r}_p - \mathbf{r}_q)], \quad (1)$$

where $\mu = 4\pi \sin \theta/\lambda$, p and q are any two atoms with scattering factors f_p , f_q and position vectors \mathbf{r}_p , \mathbf{r}_q ; $\mathbf{S} = \mathbf{s} - \mathbf{s}_0$ where \mathbf{s} and \mathbf{s}_0 are unit vectors for the scattered and incident directions respectively and $k = 2\pi/\lambda$.

Table 1. Summary of experimental measurements on liquid alloys

Radiation	Temperature (°C)	At. %Fe	First peak height (electron units)	First peak position μ (\AA^{-1})	First peak width at $\frac{1}{2}$ intensity $\Delta\mu$ (\AA^{-1})	Second peak position μ (\AA^{-1})	Intensity ratios 1st peak: 2nd peak: Dip Dip	
Cu $K\alpha$	800	2.0	170	2.72	0.48	4.84	4.17	1.95
Mo $K\alpha$	800	1.8	185	2.66	0.50	4.8	4.1	1.48
Mo $K\alpha^*$	800	0	169	2.64	0.49	4.80	4.9	1.61
Cu $K\alpha$	860	3.7	189	2.74	0.53	4.8	4.3	1.27
Mo $K\alpha$	900	1.8	185	2.68	0.51	4.8	3.9	1.47
Mo $K\alpha$	960	3.2	193	2.72	0.52	4.8	3.8	1.43
Mo $K\alpha$	1000	3.6	185	2.68	0.58	5.0	3.8	1.38
Mo $K\alpha^*$	1000	0	152	2.64	0.52	4.84	4.3	1.45
Estimates of accuracy			$\pm 10\%$	$\pm 0.03 \text{\AA}^{-1}$	$\pm 0.04 \text{\AA}^{-1}$	$\pm 0.08 \text{\AA}^{-1}$	$\pm 4\%$	$\pm 4\%$

* From Black & Cundall (1965).

For the first type of model it was assumed that each iron atom is surrounded by a number (n) of aluminum atoms held in fixed relative orientations to form a polyhedron and that these polyhedra are randomly distributed amongst the rest of the aluminum atoms (referred to below as the free aluminum atoms). When the sum in equation (1) is taken over all possible combinations of p and q then the result has the form:

$$I(\mu) = (\alpha - n\gamma)f_{\text{Al}}^2 + \gamma I_m(\mu) + \gamma(4\pi/\mu)F_2(\mu) \int_0^\infty [\varrho_{\text{Fe}}(r) - \varrho_{\text{Fe}}(0)]r \sin(\mu r) dr + (\alpha - n\gamma)(4\pi/\mu)f_{\text{Al}}^2 \int_0^\infty [\varrho_{\text{Al}}(r) - \varrho_{\text{Al}}(0)]r \sin(\mu r) dr + 2\gamma(4\pi/\mu)F_1(\mu) \int_0^\infty [\varrho_{\text{FeAl}}(r) - \varrho_{\text{Al}}(0)]r \sin(\mu r) dr \quad (2)$$

where α and γ are the respective atomic fractions of Al and Fe;

$$I_m(\mu) = \sum_p^{n+1} f_p^2 + 2 \sum_{pq}^{\frac{1}{2}n(n+1)} f_p f_q \frac{\sin \mu l_{pq}}{\mu l_{pq}}$$

is the internal contribution from a polyhedron for which pq specify all the atoms, whether iron or aluminum, and l_{pq} is the distance between any pair of atoms in the same polyhedron;

$$F_1(\mu) = f_{\text{Al}} \sum_p^{n+1} f_p \frac{\sin \mu l_{cp}}{\mu l_{cp}}$$

where l_{cp} is the distance from a polyhedron atom to the point in its polyhedron from which r.d.f.'s are measured: the term in $F_1(\mu)$ represents the contribution from interaction between free atoms and polyhedra;

$$F_2(\mu) = \sum_p^{n+1} \sum_q^{n+1} f_p f_q \frac{\sin \mu l_{cp}}{\mu l_{cp}} \frac{\sin \mu l_{cq}}{\mu l_{cq}}$$

so that the term in $F_2(\mu)$ represents the contribution from interactions between pairs of polyhedra; $\varrho_{\text{Fe}}(r)$ is the r.d.f. for a polyhedron to other polyhedra, $\varrho_{\text{FeAl}}(r)$ for a polyhedron to free aluminum atoms, $\varrho_{\text{Al}}(r)$ for a free aluminum to other free aluminum atoms and $\varrho(0)$ is the value of ϱ for $r = \infty$, and corresponds to the appropriate mean atomic density. Equation (2), and equation (4) given below, can both be derived by an extension of methods given in Chapter 11 of James (1948) and the derivations are given in full in Cundall

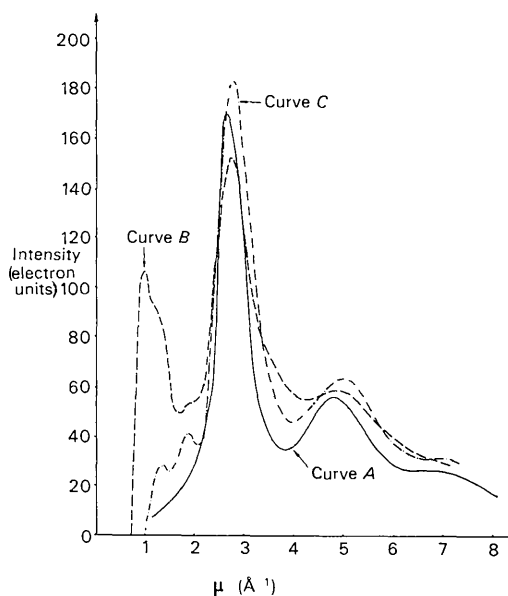


Fig. 2. Intensity curve of pure aluminum (curve A) compared with typical calculated intensities for the two models of the liquid: curve B, polyhedral model (P1); curve C, random model (R1).

Table 2. Summary of calculated scattering for polyhedral (P) and random (R) models

Ref. No.	Main characteristics of model	At. %Fe	Inner peak		First peak			Second peak position μ (\AA^{-1})	Intensity ratios	
			Height (electron units)	Position (\AA^{-1})	Height (electron units)	Position (\AA^{-1})	Width at $\frac{1}{2}$ intensity μ (\AA^{-1})		1st peak: Dip	2nd peak: Dip
P4	As P3 with r.d.f. altered only for composition change	2.4	100	1.0	132	2.6	0.85	4.5	2.35	1.05
P3	As P1 with r.d.f. distances greater and oscillations damped	5.0	205	1.0	128	2.7	0.85	4.5	2.18	1.03
P2	As P1 with r.d.f.'s broadened	4.0	140 +100	0.9 +1.3	140	2.65	0.72	4.8	2.48	1.05
P1	9-point polyhedra r.d.f. as L	4.0	107	1.0	152	2.75	0.58	4.9	2.74	1.07
L	Experimental pure Al*	0	—	—	169	2.64	0.49	4.8	4.9	1.61
R1	r.d.f. as L with short Fe-Al distances	4.0	—	—	182	2.75	0.55	5.0	3.96	1.37
R2	r.d.f. first peak larger r ; subsequent oscillations closer	5.0	—	—	166	2.70	0.88	4.7	4.61	1.94
R3	As R2 except for composition change	2.4	—	—	155	2.70	0.84	4.6	4.84	2.06

* From Black & Cundall (1965).

(1963). To compute $I(\mu)$ it is necessary to specify the composition (α, γ), the polyhedron structure (n, l_{pq}) and the three r.d.f.'s.

For the second type of model it was assumed that the iron and aluminum atoms form a random mixture. The equation for the intensity predicted by this model is:

$$I(\mu) = \alpha f_{\text{Al}}^2 + \gamma f_{\text{Fe}}^2 + \alpha(4\pi/\mu)f_{\text{Al}}^2 \int_0^\infty [\varrho_{\text{Al}}(r) - \varrho_{\text{Al}}(0)]r \sin(\mu r) dr \\ + \gamma(4\pi/\mu)f_{\text{Fe}}^2 \int_0^\infty [\varrho_{\text{Fe}}(r) - \varrho_{\text{Fe}}(0)]r \sin(\mu r) dr \\ + 2\gamma(4\pi/\mu)f_{\text{Fe}}f_{\text{Al}} \int_0^\infty [\varrho_{\text{FeAl}}(r) - \varrho_{\text{Al}}(0)]r \sin(\mu r) dr, \quad (3)$$

where ϱ_{Fe} is now the r.d.f. for iron atoms around a central iron atom, ϱ_{FeAl} the r.d.f. for all aluminum atoms around a central iron atom and ϱ_{Al} for all aluminum atoms around a central aluminum atom. The parameters that have to be specified for this model are the composition (α, γ) and the three r.d.f.'s.

The effect of variations in the model parameters

Results derived from calculations on a range of polyhedral and random models are summarized briefly in this section and the more important features will be illustrated by reference to a few selected results which are given in Table 2. Experimental data for pure aluminum are also given in this table since it is convenient to discuss both experimental and theoretical results by comparing them with those for the monatomic liquid.

Polyhedral models

Fig. 2 shows a comparison between the measured intensity for pure aluminum (curve *A*) and the intensity computed, by using equation 2, for one of the liquid models (curve *B*). For this model $\gamma=0.04$, $n=9$ and the values for l_{pq} were calculated for an ideal polyhedron based on those found in $\text{Fe}_4\text{Al}_{13}$ (Black, 1955*a, b*) with a constant Fe–Al distance of 2.48 Å. The functions

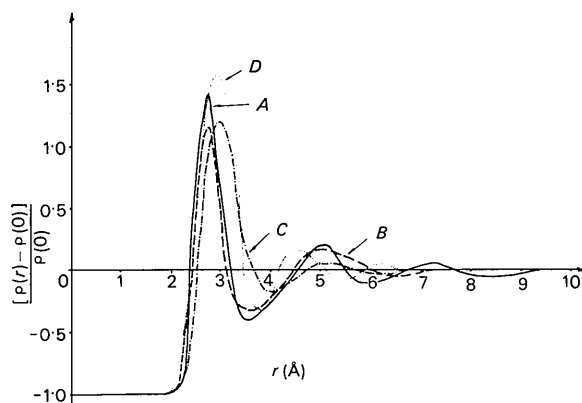


Fig. 3. Typical r.d.f.'s used in the calculations for ϱ_{Al} . *A*, used in *P1* and *R1*; *B*, used in *P2*; *C*, used in *P3* and *P4*; *D*, used in *R2*.

ϱ_{Fe} and ϱ_{Al} were based on those found experimentally for pure aluminum (Black & Cundall, 1965) with an appropriate change of scale for ϱ_{Fe} ; for ϱ_{FeAl} a curve was estimated by assuming normal Al–Al distribution for the surface atoms of the polyhedron with some sharpening of the nearest neighbour peak to account for the ordering of the neighbours on the polyhedron surface.

The two curves differ mainly in the presence of a low-angle peak in the calculated curve. This peak is built up from contributions from the ϱ_{Fe} and ϱ_{FeAl} terms; the ϱ_{Fe} term has no other significant effect on the result. The main peak (at $\mu=2.75 \text{ \AA}^{-1}$) is lower than in pure aluminum because the presence of 4% of iron involves 36% of the aluminum in polyhedra so that the ϱ_{Al} term is reduced; the ϱ_{FeAl} and the I_m terms also contribute peaks on the high-angle side of this ϱ_{Al} peak so that the resultant peak is broadened. Parameters describing this curve are listed under *P1* in Table 2. For comparison with Table 1, the peaks which correspond in position to the first and second peaks for aluminum are referred to in this table as the first and second peaks, whilst peaks at lower angles than the first are referred to as inner peaks.

The most difficult parameters to predict are the r.d.f.'s and the results did appear to be sensitive to changes in these. The two types of change that can be proposed in the short-range order represented by $[\varrho(r) - \varrho(0)]$ are in the degree of ordering and in the distances of the ordering peaks. Fig. 3 shows the r.d.f. derived experimentally for ϱ_{Al} as used in *P1* (curve *A*) and an r.d.f. in which the oscillations are of smaller amplitude and broader, which corresponds to a decrease in the ordering of the free aluminum (curve *B*). This latter curve, together with a corresponding curve from ϱ_{FeAl} , was used for model *P2*. As shown in Table 2, for this model the composite inner peak splits into two components because of a shift in the ϱ_{FeAl} contribution, whilst similar shifts in both the ϱ_{Al} and ϱ_{FeAl} contributions lower the first peak and broaden it appreciably. For *P3* the distances of the peaks used in *P2* were increased by 10% for the ϱ_{Al} and ϱ_{FeAl} curves and the amplitudes of oscillations beyond the first were decreased (curve *C*, Fig. 3); this corresponds to a liquid which is more loosely packed so that the short-range order attenuates more rapidly. The inner peak is again altered because the two contributing peaks now coincide closely, whilst relative shifts between the ϱ_{Al} and ϱ_{FeAl} contributions at higher angles smooth out the curve beyond the first peaks so that the second peak is hardly distinguishable.

The other parameters which could be varied were n , the l_{pq} and γ . A change in the value of n from 9 to 8 was shown to have only a small effect. Substantial changes in the l_{pq} could only be made by changing the mean Fe–Al distances within polyhedra; such changes were shown to affect the result significantly, but only when they were too large to be consistent with the measured density. Application of a temperature factor

to the l_{pq} also had little effect because the region of interest here does not extend to sufficiently high angles. The effect of changes in the liquid composition can be seen by comparing $P3$ with $P4$. $P4$ was computed with the r.d.f.'s of $P3$ with suitable changes to account only for the direct effect of changing γ to 0.024. The inner peak, the height of which is roughly proportional to the fraction of iron in the model alloy, changes appreciably. The first intensity peak is less sensitive to change because change in the q_{FeAl} contribution is offset by a change in the q_{Al} term.

The characteristic feature of the polyhedral model is the inner peak at about $\mu = 1.0 \text{ \AA}^{-1}$. Given that the composition and density of the liquid alloy are fixed, the height, position and breadth of this peak are functions of the values of l_{pq} , q_{Fe} and q_{FeAl} . If it could be assumed that the 'free' aluminum had the structure of pure liquid aluminum, the contribution of the q_{Al} term could be subtracted from the experimental curve and the first and subsequent peaks would then serve to test the model for q_{FeAl} independently of q_{Fe} . Unfortunately the model calculations become unreliable at low values of μ : they always predict negative values of I in the region of $\mu < 1 \text{ \AA}^{-1}$ and although the existence of the peak for $1 \text{ \AA}^{-1} < \mu < 2 \text{ \AA}^{-1}$ is in clear contrast to the prediction for other models, any attempt to obtain precise information by matching measurements in this region would demand very sophisticated model computations. The prediction of negative values for I is a symptom of a general problem with model calculations of this type which arises from the difficulty of postulating self-consistent r.d.f.'s. This difficulty is discussed below under *Inaccuracies in the calculated I at low angles*.

Random models

In Fig. 2 are shown the observed intensity for pure aluminum (curve A) and the intensity computed by equation (3) for a random model (curve C) for which the r.d.f.'s were of the form of those for the pure aluminum, modified to correspond to the short iron-aluminum contact distance required by the density. The contribution of the term involving q_{Fe} is negligibly small for a dilute liquid. The result obviously resembles that of the pure liquid more closely than those of the previous section. The q_{FeAl} term gives a main peak around $\mu = 2.9 \text{ \AA}^{-1}$ which shifts and broadens the q_{Al} contribution. However the contribution of the q_{Al} integral is now proportional to α and not to $(\alpha - n\gamma)$. There is no 'inner' peak for the model curve (the small peaks on the curve C for $\mu \approx 1-2 \text{ \AA}^{-1}$ are due to the effect of errors in the r.d.f.'s as discussed below; it is probable that they are artefacts because they have no counterpart in the experimental curves for pure aluminum which determine the main features of the random model). Parameters describing this curve are listed in Table 2 under $R1$.

Variations in the r.d.f.'s of the type discussed for $P2$ and $P3$ above were also tested for random models.

The main conclusion drawn from these tests was that the result is sensitive to changes in the mean positions of the r.d.f. peaks but comparatively insensitive to their breadth. Curve D of Fig. 3 illustrates one of the tests; this r.d.f. has a larger distance and a larger coordination number than curve A for the nearest neighbours whilst the second coordination peak is at a much shorter distance: the existence of short Fe-Al distances could allow the second Al-Al peaks to come closer on average if the liquid were well ordered. Use of this curve produced large changes ($R2$); the peaks positions were shifted and the intensity oscillations enhanced.

The results for $R3$, for which all parameters except composition were the same as those for $R2$, illustrate the effect of a composition change. The absolute heights of peaks are affected but otherwise the differences are small and in general changes in composition have much less effect in the random model than in the polyhedral model because the major contribution of the q_{Al} term is only slightly affected in the random case. Further tests showed that cut-off effects in the r.d.f.'s and removal of the anomalous dispersion corrections to f_{Fe} and f_{Al} gave comparatively small changes in the curves, so that errors in these factors in the models would not have a serious effect.

The scattered intensity from a random liquid should closely resemble that for pure aluminum provided that the form of q_{Al} is not affected by the presence of iron: any such effects would produce major changes in the scattering curve. In the absence of such effects q_{FeAl} must have a closer first coordination peak but a subsequent shape largely determined by the q_{Al} distribution, so that it would be difficult to obtain a scattering curve which differed appreciably from $R1$. This shows signs of the influence of dissolved iron by broader peaks, smaller peak to dip ratios and larger absolute heights.

A detailed attempt to fit an experimental curve to a model of this type might be made by subtracting from the observed curve a pure aluminum curve scaled to correspond to the q_{Al} contribution in equation (3). The remainder could be interpreted as due solely to the q_{FeAl} term (for a dilute alloy) and its transform would give q_{FeAl} directly. However, systematic errors in the data would have a large relative effect on the difference curve so that spurious ripples might prevent the extraction of significant detail from the r.d.f. obtained. As for the polyhedral model, detailed attempts to match any model could only be made if the possible variations in the r.d.f.'s could be specified with confidence.

Inaccuracies in the calculated I at low angles

The calculations discussed above do produce negative values of I for small μ : this is dramatic evidence that these calculations are unreliable in this region. The expression for I in equation (1) is the product of a scattered amplitude with its complex conjugate and the result must be positive. This expression can be written in the form:

$$I(\mu) = \sum_p f_p^2 + \sum_{p \neq q} \sum_q f_p f_q \cos kS \cdot \mathbf{r}_{pq} \quad (4)$$

where $\mathbf{r}_{pq} = \mathbf{r}_p - \mathbf{r}_q$. It is clear that this expression could be negative if the \mathbf{r}_{pq} were completely arbitrary quantities, but it is easily shown that it must be positive if to every member p an \mathbf{r}_p can be assigned such that $\mathbf{r}_{pq} = \mathbf{r}_p - \mathbf{r}_q$. This is the condition that the \mathbf{r}_{pq} are vectors specifying a possible configuration of points in three dimensions and negative values can only be obtained if this condition is violated. When the discrete set of \mathbf{r}_{pq} 's is replaced by an r.d.f., it is possible to violate the condition by drawing a curve which could not be obtained by averaging over the vectors connecting a three dimensional array of points. The occurrence of negative $I(\mu)$ for small values of μ must indicate that the r.d.f.'s are inconsistent at the larger values of r , because the transform integrals of equations (2) and (3) above are sensitive to the precise shape of $\varrho(r)$ for large r if μ is small.

Any r.d.f. can be checked roughly by simple attempts to visualize it in terms of a three-dimensional array of points and such checks will ensure that it is to a first approximation geometrically self-consistent, but there does not appear to be any simple analytic test which can be used to establish this self-consistency more rigorously. For a monatomic liquid, the condition that $I(\mu)$ be positive is a test of this type because it is equivalent to the condition that $\varrho(r)$ be geometrically consistent. Furthermore, in the case of a composite liquid there should be further self-consistency conditions between the various r.d.f.'s (in this case ϱ_{Fe} , ϱ_{Al} and ϱ_{FeAl}) involved. No useful analytic conditions of this type have been derived or applied for testing the r.d.f.'s used in the present work. Thus, curves such as *B*, *C*, *D* in Fig. 3, although they are r.d.f.'s which have

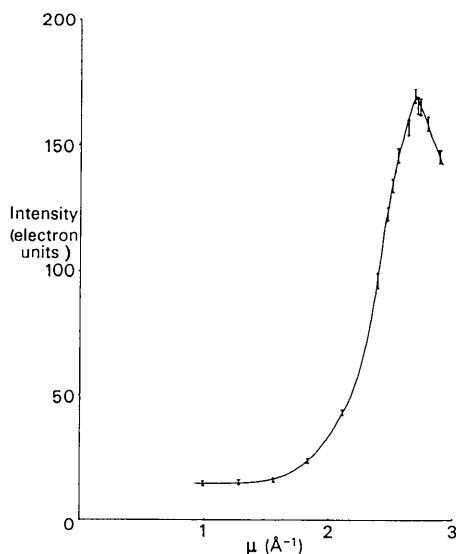


Fig. 4. The low-angle region of the intensity curve for a liquid alloy containing 2.0 at. % Fe at 800°C, showing experimental points with their statistical probable errors.

been approximately tested for self-consistency and do incorporate the features described above under *Polyhedral models* and *Random models*, cannot be proposed as accurately self-consistent representations of model liquids.

There is another self-consistency condition on $\varrho(r)$, that it must correspond to the correct total number of atoms, but this is not a stringent condition because gross errors for small r can be compensated by quite small changes at large r , and this 'corrected' curve would give an inaccurate transform.

Discussion and comparison with experiment

Comparison of the *P* and *R* results in Table 2 shows that although large variations in predicted scattering can be obtained by varying the input parameters of each type of model, there are nevertheless overall differences between the two which persist even when the input parameters are subjected to extreme variations. This generalization is supported by the full range of model computation results (Cundall, 1963) and the overall differences can be summarized, and compared with the main features of the experimental results in Table 1, as follows:

(1) All polyhedral models show one or two peaks around $\mu = 1 \text{ \AA}^{-1}$, which have no counterpart for the random models. They are much larger than and so dominate the spurious effects produced by the r.d.f. errors discussed above under *Inaccuracies in the calculated I at low angles*. These low-angle peaks are to be expected from the polyhedral model because of the larger regular interatomic distances involved. No evidence of such low-angle peaks was found in any of the alloy scattering curves. Fig. 4 shows in detail the low-angle region of one of these curves; there is no low-angle peak of height larger than five units, compared with a peak of at least seventy units predicted in Table 2.

(2) The peak to dip ratios and the peak heights for the *R* curves lie in a different range from those for the *P* curves; in this respect the experimental curves agree with the random model.

(3) The first peak for the alloy curves tends to be of greater height than, and to occur at larger μ than, the pure aluminum peak. Both *R* and *P* models predict the increase in μ , because of the shorter interatomic distances involved, but only the *R1* and *R2* curves give the increased height.

(4) Peak breadths are greater than for pure aluminum for all the models, but only for *P1* and *R1* are the breadths sufficiently small to be consistent with the measurements. These are the curves for which the r.d.f.'s are in closest agreement with experimental results for aluminum.

Thus the alloy measurements indicate a structure very like that of pure aluminum; the differences from the pure aluminum scattering found experimentally closely resemble those given by computations based on a model in which the only change from the pure liquid

r.d.f.'s is that shortened iron-aluminum distances are incorporated in Q_{FeAl} . The changes with composition found experimentally are consistent with those predicted by the random model; the changes with temperature are similar to the changes for pure aluminum. It would be possible to proceed further with our results to attempt to extract more detailed information about Q_{FeAl} by attempting to fit $R1$ more closely to the data. It is likely however that such detail would be spurious because of the existing errors in the r.d.f.'s and the difficulty of postulating consistent and significant changes in them.

The models of polyhedral and random liquids can be regarded as the two extremes of a whole range of possible model liquids. The polyhedron model could be considered as a special version of the random model which gave unusually sharp peaks at specific values of r in the Q_{Al} and Q_{FeAl} curves, and the range of models could be realized by gradually smoothing out these peaks. However, the survey above indicates (for example in the absence of any inner peak more than 7% of the smallest prediction by a polyhedron model) that adequate agreement could only be obtained with models very near to the random end of this range, and the differences between theory and experiment do not point systematically to any modification of $R1$ to include features of the polyhedral model. Accordingly, such 'intermediate' models have not been investigated.

Conclusion

Two main conclusions emerge from this work. The first is that polyhedral units do not persist in the liquid alloys at temperatures more than 50°C above the liquidus. The significance of this has already been discussed in the *Introduction*. The polyhedral units in the solid are probably secondary features in structures whose main feature is the accommodation of short distances between the transition metal and aluminum atoms. In so far as the structures depart from the close packing of atoms of unequal radii (Black, 1956) this must occur in order to produce favourable bond angles for particular links in the structure (Brown, 1959, 1962).

The second set of conclusions concerns the prospect of obtaining detailed information about multi-component liquid systems. The difficulties arising from systematic errors in the experimental data, which we have discussed elsewhere (Black & Cundall, 1965), are not of critical significance here. The main limitation is the difficulty of postulating the various r.d.f.'s required to specify a complex structure in such a way that they are geometrically self-consistent and mutually consistent so

that they correspond to specified physical features. If extensive model calculations using Monte Carlo methods (see e.g. Fisher, 1964; Bernal, 1959) could be made on a two-component system then the range, character and significance of possible variations in the r.d.f.'s might be better understood. It would then be worth proceeding with systematic methods of fitting observed to calculated scattering curves.

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