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The crystal structure of the ternary alloy α(AlFeSi).

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The crystal structure of the phase α(AlFeSi) has been determined from visually estimated X-ray intensities. Starting with the atomic coordinates of the near isomorph α(AlMnSi) the structure was refined by three-dimensional Fourier and difference syntheses. There are 138 atoms in the cubic unit cell, $a = 12{\cdot}56$ Å, space group *Im*3. There is evidence that certain atomic sites are only partially occupied. No attempt has been made to distinguish between aluminum and silicon.

Description of the phase

In a recent paper Cooper & Robinson (1966) reported the structure determination of the ternary phase α(AlMnSi). This note describes the refinement of a near isomorph in the Al–Fe–Si system. The crystals which were kindly provided by Aluminium Laboratories, Banbury, contained some manganese as impurity. The chemical composition as determined by microprobe analysis corresponded to the formula $Fe_4MnSi_2Al_{19}$ which is close to the composition $Fe_5Si_2Al_{20}$ reported by Phragmen (1950) for an isomorph in this system if it is assumed that manganese substitutes for iron.

The density of the crystals was determined by flotation to be 3.59 ± 0.06 $g.cm^{-3}$, which agrees with the calculated value of 3.62 $g.cm^{-3}$ for an ideal cell made up of 100 Al, 14 Si and 24 Fe atoms. The cell side, obtained by the method of Farquhar & Lipson (1946) was 12.56 ± 0.02 Å in accord with the value 12.548 Å obtained by Phragmen (1950). The Laue group is *m*3, and reflexions for which $h+k+l$ is odd were absent in contrast to the situation in α(AlMnSi) where they were present but weak.

The structure refinement

The intensities of reflexions to a maximum h and k of 15 and l of 3 were estimated visually with the use of Mo $K\alpha$ radiation and Weissenberg multiple film technique. Altogether 225 observed reflexions (maximum $\sin\theta/\lambda = 0.8$) were employed in the refinement together with their equivalent reflexions. Lorentz and polarization corrections were applied. The absorption corrections for the small crystal fragment used were constant to within 2 % for all observed reflections and were therefore not applied. A three-dimensional Fourier program written by Mrs J. C. Matthewman was used for the refinement, the scattering factors being calculated from the analytic approximation of Forsyth & Wells (1959). Extinction was allowed for in the five strongest reflexions by replacing them by their calculated values in the computation of atomic shifts.

The refinement was begun with the coordinates of α(AlMnSi) – space group *Pm*3 – although it was expected that the lattice would be more nearly body centred. The main deviation from body centring in α(AlMnSi) arises from the occupation of site Al(7) but not Al(8) (see Table 1); all other pairs of atoms are approximately related by a translation of $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Inspection of the Fourier and difference maps for a section of the unit cell at $z = 0$ showed that both Al(7) and Al(8) sites were occupied in α(AlFeSi). The peak heights indicated 50 % occupation of each site. It was also observed that the atom Al(9) had two equally probable sites and the scattering power was accordingly split between the sites Al(9) and Al(10). The refinement continued until no significant features remained on the difference maps, at which stage the R value was 0.10.

A consideration of the bond lengths showed that the crystal must be composed of two types of unit cell. In the one, sites Al(7), Al(9) and Al(11) are occupied and in the other sites Al(8), Al(10) and Al(12) are occupied (see Table 1). The average structure belongs to the space group *Im*3

Table 1. *Comparison of atomic positions in* α(AlFeSi) *and* α(AlMnSi)

Atom	α(AlFeSi) cell I			α(AlFeSi) cell II			α(AlMnSi)		
site	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Fe(1) or Mn(1)	0·3243	0·1981	0	0·3243	0·1981	0	0·3271	0·2006	0
Fe(2) or Mn(2)	0·1757	0·3019	0·5	0·1757	0·3019	0·5	0·1797	0·3085	0·5
Al(1)	0·3777	0	0	0·3777	0	0	0·3638	0	0
Al(2)	0·1223	0·5	0·5	0·1223	0·5	0·5	0·1216	0·5	0·5
Al(3)	0·1651	0·1006	0	0·1651	0·1006	0	0·1636	0·0997	0
Al(4)	0·3349	0·3994	0·5	0·3349	0·3994	0·5	0·3342	0·3990	0·5
Al(5)	0·1146	0·1872	0·3003	0·1146	0·1872	0·3003	0·1185	0·1892	0·2980
Al(6)	0·3854	0·3128	0·1997	0·3854	0·3128	0·1997	0·3897	0·3127	0·1955
Al(7)	0·2990	0	0·5	—	—	—	0·2897	0	0·5
Al(8)	—	—	—	0·2010	0·5	0	—	—	—
Al(9)	0·3266	0·4030	0	—	—	—	0·3319	0·4037	0
Al(10)	—	—	—	0·3725	0·3830	0	—	—	—
Al(11)	0·1275	0·1170	0·5	—	—	—	0·1205	0·1175	0·5
Al(12)	—	—	—	0·1734	0·0970	0·5	—	—	—

although each type of unit cell, when considered separately, is primitive.

The standard deviations of the atomic coordinates were less than 0.002 Å for iron atoms and less than 0.004 Å for aluminum atoms, with the exception of atom Al(9) for which $\sigma(x)=0.020$ Å. In the absence of more accurate data no detailed understanding of the occupation of sites in the alloy can be obtained. The existence of the sites listed in Table 1 does, however, appear to be well established.

The atomic environments in both types of unit cell can be described in similar terms to those in α(AlMnSi) which have been discussed by Cooper & Robinson (1966). The transition metal coordination polyhedra contain one extremely short manganese or iron to aluminium bond. In α(AlMnSi) these bonds were 2.43 and 2.27 Å long for the 10-fold and 9-fold coordinated polyhedra respectively; in α(AlFeSi) the equivalent bond is 2·34 Å in both polyhedra. Abnormally short bonds are a well-known feature of transition metal-aluminium polyhedra and have been discussed elsewhere (*cf.* Black & Taylor 1958).

A more detailed account of the structure of this alloy, together with tables of observed and calculated structure factors, will appear in a dissertation to be submitted to the University of Cambridge by the author.

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References

BLACK, P. J. & TAYLOR, W. H. (1958). *Rev. Mod. Phys.* **30**, 57.
COOPER, M. & ROBINSON, K. (1966). *Acta Cryst.* **20**, 614.
FARQUHAR, M. & LIPSON, H. (1946). *Proc. Phys. Soc.* **58**, 200.
FORSYTH, J. B. & WELLS, M. (1959). *Acta Cryst.* **12**, 412.
PHRAGMEN, G. (1950). *J. Inst. Met.* **77**, 489.

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Structure factors and Debye–Waller factors of sodium chloride at 300°K, 202°K and 78°K.

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Structure factors of sodium chloride have been measured by the X-ray powder diffraction method. The values of Debye–Waller factors were determined and compared with results of theoretical calculations by Buyers and Smith, and with earlier experimental results.

Introduction

Sodium chloride is the ionic crystal subjected to the most extensive studies by the X-ray diffraction method. However, the results of Renninger (1952), Witte & Wölfel (1955), Schoknecht (1957) and Vihinen (1960), which have been usually considered to be very accurate, differ considerably from those of more recent experimental and theoretical studies by Levy, Agron & Busing (1963), Abrahams & Bernstein (1965), Buyers & Smith (1964) and Pryor (1966). These discrepancies urged us to make an independent study of the structure factors of sodium chloride. In this work the measurement was extended to lower temperatures and the temperature dependence of Debye-Waller factors was also studied.

Experimental conditions

Intensity measurements were performed with a relative method with monochromatized Cu $K\alpha$ radiation. The integrated intensities at low temperatures were measured relatively to the room temperature values. High purity sodium chloride powder was ground until the particle size became about 1–2μ. By preliminary measurements it was proved that under a moulding pressure of 30 kp.cm^{-2} the integrated intensities were independent of specimen preparation. At higher pressures, there occurred appreciable increase in the ratio of integrated intensities, $I(h00)/I(hh0)$, apparently due to the preferred orientation. For final measurements the samples were packed into a sample holder applying pressures between 5 and 30 kp.cm^{-2}. By the texture goniometry, these samples were shown to be free from preferred orientation to one per cent.

The line broadening due to the strain in heavily ground particles may cause errors in the estimation of background. To study this, high angle reflexions of ground samples were compared with those of a sample made of a very fine sedimented powder, and it was shown that the integrated intensities were not affected by heavy grinding.

Results and discussion

The measured integrated intensities were corrected for temperature diffuse scattering (TDS) (Suortti, 1967). The scale factor was determined by putting the value of the structure factor, $F(220)$, at room temperature equal to the absolute value 16.85 measured by Witte & Wölfel (1955). The results obtained are given in Table 1, together with estimated errors, δF, due to the intensity measurements.

The Debye–Waller factors, B(Na) and B(Cl), of the individual ions at each temperature were determined on the assumption that the experimental and calculated structure factors coincided at high values of $\sin\theta/\lambda$, by employing