A study of the magnetic structures of chromium–silicon solid solutions

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Abstract. The antiferromagnetic structures of Cr–Si solid solutions in the range 1·5–6·0 at% Si have been studied by neutron powder diffraction. The results confirm that the commensurate antiferromagnetic structure is stabilised at around 1·8 at% Si. Both the magnetic moment and the Néel temperature are found to decrease with increasing silicon content and tend to zero at about 7·2 at% Si. There is some evidence that the magnetic electrons are of E_g symmetry and it is suggested that the reduction of magnetic moment is due to the stabilisation of the I_{2g} relative to the E_g electrons in the chromium band brought about by the formation of covalent bonds with silicon.

1. Introduction

The effect of alloying on the spin-density wave in chromium has been the subject of much experimental and theoretical interest. In general the addition of a transition element with more d electrons than chromium is to increase the Q vector, the Néel temperature and the average moment. This behaviour can be explained qualitatively in terms of the model proposed by Lomer (1962) for the stability of the spin-density wave. In this two-band model the effect of increasing the electron-to-atom ratio by an electron-rich solute is to expand the electron surface relative to the hole octahedra thus increasing the propagation vector Q corresponding to the shortest vector separating the two parallel pieces of Fermi surface. Only a small increase in the electron concentration (about 1% for Cr–Pt, Cr–Mn) is sufficient to stabilise the commensurate ($|Q| = 2\pi/a$) antiferromagnetic structure. Below this critical concentration commensurate and incommensurate phases may co-exist. In an extension of Lomer's model Fedders and Martin (1966) showed that the Néel temperature should depend exponentially on the area of the parallel pieces of Fermi surface and hence be sensitive to alloying. This simple interpretation appears to be valid for small concentrations of most of the transition metals alloyed with chromium. The notable exceptions are the Cr–Fe and Cr–Co systems for which it is supposed that the existence of local moments destroys the validity of the model.

Studies of the effect of additions of aluminium to chromium (Kallel and de Bergevin 1967, Costa and Brown 1977) suggest that aluminium acts as an electron donor since except for concentrations less than 1% its effect is to increase the characteristic

magnetic properties. However, arguments involving the donation of s and p electrons to the chromium d band cannot completely account for variations in charge and spin density on alloying.

It seems likely that this demonstrates a breakdown in the rigid band model. To investigate this problem further we have undertaken a new study of the Cr–Si system to compare the effect of a 4B element, silicon, with that of the 3B element aluminium. Previous investigations of the magnetic and electrical properties of dilute alloys of silicon and chromium (Jayaraman *et al* 1976, Arajs *et al* 1971, Hedman and Åström 1975) show an increase in the characteristic properties and were interpreted as evidence that silicon donates s and p electrons to the chromium d band. Previous neutron diffraction measurements (Cable 1977) confirmed the stability of the commensurate phase for silicon additions above 1·8 at% and were interpreted as showing an increase in the average chromium moment over that in pure chromium but accompanied by a depression of the Néel temperature. In spite of his finding conflicting changes in $|Q|$ $\bar{\mu}$ and T_N for addition of silicon, Cable interpreted his results in terms of a rigid band model. He argued that, when the impurity is a B subgroup element its excess of s and p electrons is screened by the host atoms, so that in this case charge is always transferred from diluant to matrix atoms.

The conflicting behaviour of the characteristic properties justify further investigation of the chromium–silicon system. In this paper we report neutron diffraction measurements made over a wider range of composition than those of Cable.

2. Experimental procedure

Neutron powder diffraction diagrams were measured for chromium alloys containing 1·5, 2·0, 2·5, 3·0, 4·5 and 6·0 at% silicon. The more dilute alloys were lent to us by Professor A Oles of the Institute of Physics and Nuclear Techniques, Cracow, Poland. The more concentrated alloys were made for us by Dr J G Booth of the University of Salford from 5N purity constituents. Chromium annealed at 1000 °C can contain up to 7·5 at% Si substitutionally (Pearson 1958); the addition results in a contraction of the lattice from 2·8848 to 2·8826 Å. X-ray examination showed that our samples were single phase BCC alloys to the limits of detection.

The neutron diffraction measurements were made using the D2 diffractometer at ILL, Grenoble. A neutron beam of 1·7 Å wavelength diffracted by the (111) planes of a germanium monochromator was used so that higher order contamination of the beam was avoided. The samples were contained in thin-walled vanadium cans in a variable temperature cryostat and cooled with helium vapour. The temperature of the sample was measured to better than 0·1 K using a silicon diode in thermal contact with the specimen can. In each pattern the intensities of one nuclear and three magnetic reflections were measured with good accuracy at 4·2 K. The Néel temperatures of the samples containing 4·5 and 6 at% Si were established by following the intensity of the 100 reflection as a function of temperature.

3. Results

Each of the five alloys with highest silicon content gave diffraction patterns consistent with a simple commensurate antiferromagnetic structure. The pattern for the 1·5 at%

alloy showed two magnetic satellite reflections one on either side of the 100 peak, indicating the presence of an incommensurate phase at 4·2 K. The separation of the satellites gave $|Q| = 0.966$ $(2\pi/a)$; their intensities were about one-fifth that of the central peak. A pure antiferromagnetic phase in the transverse spin density wave (TSDW) structure gives satellites whose intensity is half that of the central peak. Departures from this ratio are observed if a proportion of the material is in the commensurate phase or in the longitudinally polarised state (LSDW). The LSDW state does not give resolved satellite reflections in a powder pattern. In the 1·5 at% Si alloy the intensity ratio suggests a mixture of TSDW and commensurate phases. This mixture rather than one involving the LSDW is suggested by the phase diagram of Cable (1977).

The absolute intensities of the 100, 111, and 210 magnetic reflections were obtained after correction for the Lorentz and geometrical factors by normalisation to the 110 nuclear intensity. Both absorption and temperature factors varied negligibly over the range of scattering angles involved. The nuclear scattering lengths 3·63 fm for chromium and 4·13 fm for silicon (Bacon 1975) were used. The relationship used was

$$F_{\text{mag}}(hkl) = 2\bar{b} \left\{ \frac{j_{110} \sin \theta_{hkl} \sin 2\theta_{hkl} I_{(hkl)\text{obs}}}{j_{hkl} \sin \theta_{110} \sin 2\theta_{110} I_{(110)\text{obs}}} \right\}^{1/2}.$$

In this equation $\bar{b}$ is the average scattering length associated with the alloy, j is the multiplicity of the reflection, θ the Bragg angle and I_{obs} the measured integrated intensity. The average magnetic moment can be calculated from

$$\bar{\mu} = \frac{mc^2}{e^2 \mu_{\text{N}}} \frac{1}{\langle q^2 \rangle^{1/2}} \frac{F_{\text{mag}}(hkl)}{f(hkl)}$$

where $f(hkl)$ is the form factor and $q^2 = \sin^2\alpha$, α being the angle between the spin direction and the scattering vector. For the commensurate structure $\langle q^2 \rangle = 2/3$. The three magnetic structure factors obtained for each concentration were used to derive both a mean magnetic moment μ and the fraction γ of magnetic electrons in E_{g} states. The form factors used were $\langle j0 \rangle$ and $\langle j4 \rangle$ calculated for 3d electrons in the $3d^4 4s^2$ and $3d^4$ configurations respectively (Freeman and Watson 1961, Watson and Freeman 1961).

The results are summarised in table 1. The moment values derived are sensitive to the form factor $\langle j0 \rangle$ and hence to the configuration assumed. Calculations based on

Table 1. Magnetic moments (μ) per chromium atom and fraction of the magnetic electrons in E_{g} orbitals (γ). In column 2 the superscript $\pm$ refers to the satellite reflections observed on either side of the 100 reflection for the composition Cr–1·5 % Si.

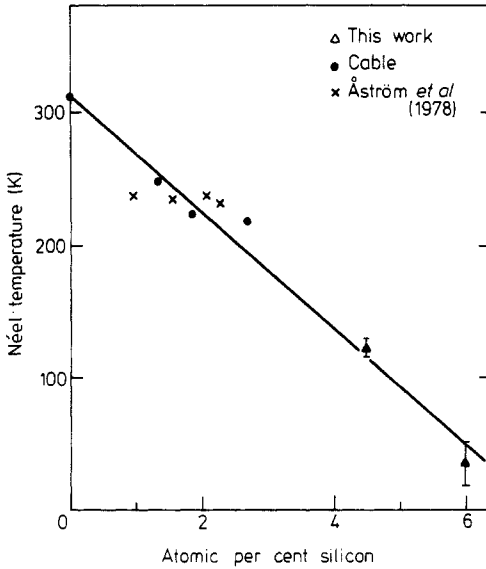| Silicon content (at%)	$jF^2(10^{-24}\ \text{cm}^{-2})$			Q	$\bar{\mu}$ (μ_{B})	μ_{WS} (μ_{B})	γ
	100	111	210				
1·5	0·016⁻ 0·079 0·015⁻	0·076	0·048	0·966	0·556 ± 0·02	0·55 ± 0·02	0·22 ± 0·15
2·0	0·171	0·086	0·052	1	0·574 ± 0·01	0·568 ± 0·01	0·21 ± 0·12
2·5	0·162	0·078	0·098	1	0·567 ± 0·01	0·56 ± 0·01	0·16 ± 0·14
3·0	0·136	0·075	0·054	1	0·52 ± 0·02	0·515 ± 0·02	0·12 ± 0·10
4·5	0·063	0·04	0·026	1	0·35 ± 0·02	0·347 ± 0·02	0·02 ± 0·1
6·0	0·007	0·005		1	0·12 ± 0·03	0·11 ± 0·03	

Figure 1. Variation of Néel temperature with silicon content.

the chromium $3d^6$ configuration were made but showed that this form factor gives a much worse fit to the data. It should also be emphasised, as shown by Costa and Brown (1977), that although different chromium configurations may yield different moments by extrapolation to $\sin \theta/\lambda = 0$ these differences are minimal if the real moment is taken as that within the Wigner–Seitz cell. This value μ_{WS} is also given in table 1.

Figure 2 shows the mean moment plotted as a function of silicon content. It is evident that initially the moment remains essentially constant but that beyond about $2 \cdot 5$ at% Si it decreases rapidly tending to zero at $7 \cdot 2$ at%. For comparison the variation of γ is also plotted on the same figure. In figure 1 data from several sources giving the variation of Néel temperature with composition are plotted; a rapid decrease with increasing silicon content is observed.
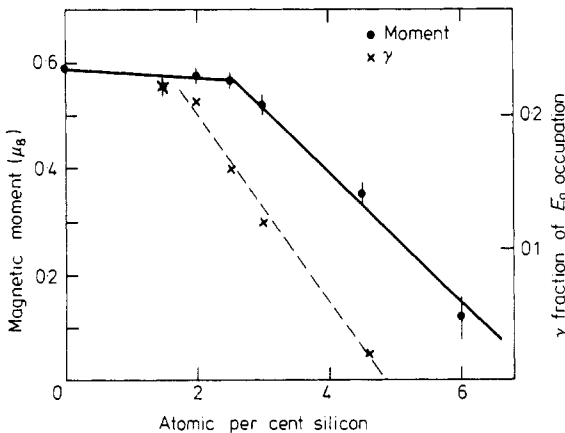

Figure 2. Variation of magnetic moment and the occupation of E_g orbitals (γ) as a function of silicon content.

4. Discussion

We may compare our results with those of Cable (1977) for the limited range of composition covered by his experiments. It is established that the commensurate antiferromagnetic phase is stable at 4·2 K for silicon contents greater than 1·8 at%. For low silicon contents, at least up to 0·9 at%, the pure TSDW structure is found but at intermediate compositions 1·32 at% (Cable 1977) and 1·5 at% a mixture of the TSDW and commensurate phases is present. This mixture could arise from fluctuations in composition but more probably is due to the formation of domains and their pinning by imperfections. The decrease in Néel temperature with composition found by Cable is borne out by our measurements and at concentrations above 2·5 at% Si follows the decrease in the magnetic moment to extrapolate to zero at 7·2 at%. Our magnetic structure factors are also in reasonable agreement with those of Cable; however our derived moments are smaller by a factor of two. Thus we conclude that the overall effect of adding silicon to chromium is to stabilise the commensurate structure, decrease the Néel temperature and for compositions beyond 2·5 at% to reduce the magnetic moment. On the basis of these results it is timely to reconsider the rigid band arguments previously put forward to explain the magnetic and transport properties of the dilute (<2 at%) alloys.

The behaviour of the characteristic properties of chromium as silicon is added is not straightforward. The increase of $|Q|$ at low silicon contents and the rapid establishment of a commensurate structure suggest an increase in the electron concentration. However the diminution of the magnetic moment and the drop in the Néel temperature are characteristic of the addition of an electron acceptor impurity. It is clear therefore that the simple model which explains the properties of the transition metal chromium alloys is not applicable to the silicon–chromium system. Jayaraman *et al* argue that silicon may act as an interstitial impurity, contributing s and p electrons to the chromium d band which would be involved in covalent bonding if the silicon entered substitutionally. In the absence of direct evidence such as density measurements this hypothesis seems unlikely in view of the atomic radius of silicon which is larger than that of chromium. Furthermore there is evidence (Pearson 1958), which was confirmed by measurements on our alloys, that the chromium lattice contracts with increasing silicon content. The concentration around 1·8 at% at which the commensurate phase is stabilised is consistent with the critical excess electron concentration (0·061 electrons per atom) observed in other systems, e.g. CrRe (Lebech and Mikke 1972) and CrPt (Booth *et al* 1978) assuming that silicon donates between 3 and 4 electrons per atom to the chromium d band. Within the rigid band approximation such a donation is not consistent with the reduction in both the magnetic moment and Néel temperature.

At first sight the behaviour of Cr–Si and Cr–Al alloys appears to be contradictory. In both cases the commensurate phase is rapidly stabilised but in the aluminium alloys this stabilisation is accompanied by an increase in moment and in Néel temperature whereas for the silicon alloys the reverse is true. Some further insight can be obtained from the variation of γ, the fraction of unpaired electrons in E_g orbitals. Although the limitations of the data place severe restrictions on the accuracy there is a tendency for γ to increase with the addition of aluminium and to decrease with the addition of silicon. Taken with the respective magnetic moment variations this suggests that the magnetic electrons have E_g symmetry. For aluminium alloys x-ray data suggest that the aluminium electrons enhance the T_{2g} electron density (Costa and

Brown 1977) but the strength of any covalent bonds formed is insufficient to prevent the expansion of the lattice. It was suggested that the consequent reduction of d shell overlap was responsible for narrowing the d band with a consequent increase in magnetic moment. A similar mechanism may be responsible for the behaviour of the silicon–chromium alloys but with the difference that the tendency to form covalent bonds is stronger. This is shown by the slight contraction of the lattice. If silicon enters the chromium lattice substitutionally its s and p electrons will overlap most strongly with the chromium T_{2g} electrons. The covalent bond formation will therefore lower the energy of the T_{2g} electrons relative to the E_g electrons with a consequent increase in bandwidth and reduction in the number of magnetic electrons.

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