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## Magnetic phase diagram of $(\text{Cr}_{0.97}\text{Mo}_{0.03})_{1-x}\text{Si}_x$

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**Abstract.** The magnetic phase diagram of  $(\text{Cr}_{0.97}\text{Mo}_{0.03})_{1-x}\text{Si}_x$  was determined from electrical resistivity measurements. Mo was found to suppress completely the commensurate spin-density wave phase in the  $\text{Cr}_{1-x}\text{Si}_x$  system. The concentration dependence of the Néel temperature is well accounted for by theory.

### 1. Introduction

The Cr–Si system has a complex magnetic phase diagram consisting of a commensurate (c) spin density wave (SDW) region, an incommensurate (i) SDW region appearing at low Si concentrations, and a paramagnetic region (Alberts and Lourens 1988). A triple point exists near 1 at. % Si and 230 K where the above three states co-exist. The first order CSDW–P transitions are characterised by large discontinuities in the physical properties of Cr–Si (Alberts and Lourens 1988). The ISDW–P transitions are continuous. First order CSDW–P transitions are also observed (Suzuki 1976) in Cr–Fe alloys and are successfully accounted for by the theory of Nakanishi and Kasuya (1977) which is valid for systems like Cr–Fe with localised moments on Fe, where the sequence of phase changes near the triple point is from P to ISDW to CSDW. The case of Cr–Si where localised moments on Si are not expected, is, however, at present not well understood as was recently shown by Alberts and Lourens (1988) that the sequence of phase transitions in this system near the triple point is from P to CSDW to ISDW instead of P to ISDW to CSDW as for Cr–Fe.

The complex nature of the magnetic phase diagram of Cr–Si was attributed by Endoh *et al* (1982) to the particular way in which Si impurities act as electron donors in Cr. Si impurities with an electron to atom ratio smaller than that of Cr do not act as simple electron donors like others (e.g. Mn for which the electron to atom ratio is larger than that of Cr), but rather give rise (Endoh *et al* 1982) to a negative electron reservoir from which electrons are supplied to the magnetic bands. The electron reservoir plays an active role in stabilising the CSDW state at concentrations above  $\sim 1$  at. % Si.

No theory exists to calculate the positions of all the transition lines, i.e. the second order ISDW–P, the first order CSDW–P and the ISDW–CSDW phase lines, on the magnetic phase diagram of the Cr–Si system. Dadârlat *et al* (1980) used a Fedders–Martin (1966)-type two-band model as an approximation to calculate Néel temperatures ( $T_N$ ) of Cr–Si alloys by taking account of the scattering effect caused by the Si impurities as well as of the effects of distortions of the Fermi surface which give rise to changes in the density of states. The scattering effect introduces a pair-breaking mechanism that always lowers

$T_N$ . Dadârlat *et al* (1980) show (see also Crisan and Anghel 1976) that distortions of the Fermi surface can lead to an increase in  $T_N$ . They combined these two effects to explain the anomalous behaviour of  $T_N$  with increasing Si content, namely a near linear decrease of  $T_N$  up to  $\sim 1$  at. % Si (i.e. in the ISDW phase) followed by a slight increase in the CSDW phase with a minimum near 1 at. % Si. A good fit between theory and experiment was obtained. It must however be kept in mind that the increase of  $T_N$  for concentrations  $c > 1$  at. % Si is associated (Endoh *et al* 1982) with a phase change from the ISDW to the CSDW phase, due to the influence of the electron reservoir. ISDW-CSDW phase changes are, however, not included in the theory of Dadârlat *et al* (1980). If the Cr-Si system could be tailored to suppress the formation of the CSDW phase completely, leaving the system in only one SDW state at all Si concentrations, the system should be less complex, thus allowing a direct comparison between theory and experiment.

When Mo, which is isoelectronic with Cr, is added to Cr the system remains Cr-like (ISDW) up to high Mo concentrations (Cywinski and Hicks 1986). Mo acts to vary the strength of the SDW in Cr and the Cr-Mo system can be regarded to first order as a 'weakened' Cr (Ström-Olsen and Wilford 1980). We found that adding a small amount of Mo to Cr-Si completely suppresses the CSDW state making  $(\text{Cr}_{0.97}\text{Mo}_{0.03})_{1-x}\text{Si}_x$  a suitable system for application of the theory of Dadârlat *et al* (1980). We report here a study of the magnetic behaviour of  $(\text{Cr}_{0.97}\text{Mo}_{0.03})_{1-x}\text{Si}_x$  and found that the magnetic phase diagram of this system is well accounted for by their theory.

## 2. Experimental procedure

$(\text{Cr}_{0.97}\text{Mo}_{0.03})_{1-x}\text{Si}_x$  alloys with  $x = 0.003, 0.005, 0.01, 0.015, 0.02$  and  $0.025$  were prepared from 99.99% Cr and Mo and 99.999% Si by arc melting. The alloys were homogenised at 1000 °C for 3 days. X-ray diffraction methods revealed only BCC lines without any trace of extra phases in all the samples. Electron microprobe analyses showed the samples to be of good homogeneity and concentrations determined by atomic absorption and induction coupled plasma (ICP) atomic emission techniques compare well with the nominal concentrations quoted above.

The magnetic transition temperatures were monitored by measuring the electrical resistivity ( $\rho$ ) of the samples as a function of temperature at 0.5 K intervals in the temperature range 4–500 K. The anomaly in the  $\rho$ - $T$  curves was used to define  $T_N$ .  $\rho$  was measured using standard four-probe methods described previously (Smit and Alberts 1987).

## 3. Results

Two typical examples of  $\rho$ - $T$  curves are shown in figure 1 for  $x = 0.005$  and  $0.015$ . Well defined anomalies very similar to those observed for other Cr alloys (Smit and Alberts 1987), were observed near  $T_N$ .  $T_N$  was defined, as usual (Smit and Alberts 1987), as the temperature where  $d\rho/dT$  is a minimum. Two typical examples are also shown in figure 1. Figure 2 shows the  $d\rho/dT$  versus  $T$  curve for a  $\text{Cr}_{1-x}\text{Si}_x$  sample with  $x = 1.4$  at. % Si. It is known from the magneto-elastic data of Alberts and Lourens (1988) that both CSDW-P (at  $T_N$ ) and ISDW-CSDW (at  $T_{IC}$ ) transitions should occur for this sample. The value of  $T_{IC}$  obtained from their magneto-elastic data is also shown in figure 2. In this figure  $d\rho/dT$  displays a sharp minimum at  $T_N$  followed by a much shallower one, situated on a

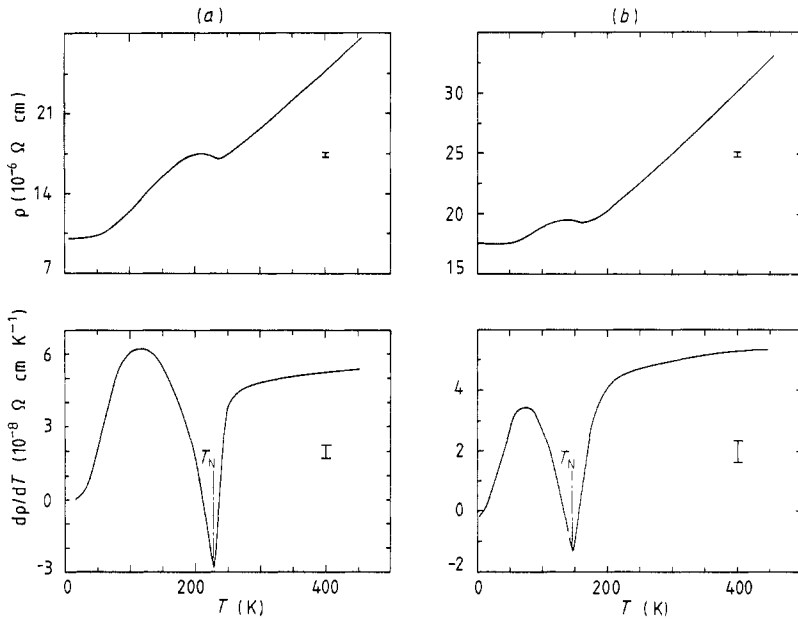


Figure 1. Temperature dependence of  $\rho$  and  $d\rho/dT$  for  $(\text{Cr}_{0.97}\text{Mo}_{0.03})_{1-x}\text{Si}_x$  with (a)  $x = 0.005$  and (b)  $0.015$ .

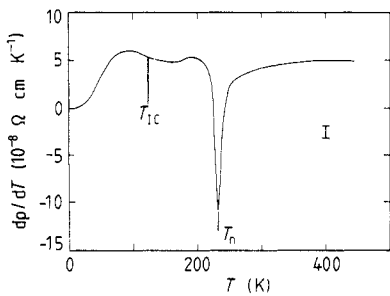


Figure 2. Temperature dependence of  $d\rho/dT$  for  $\text{Cr}_{1-x}\text{Si}_x$  with  $x = 1.4$  at. % Si. The value of  $T_{IC}$  was taken from the work of Alberts and Lourens (1988).

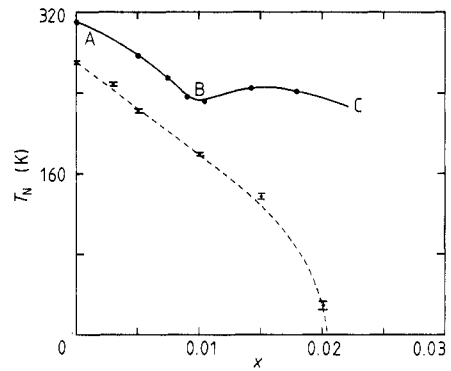


Figure 3. Variation of the Néel temperatures of  $(\text{Cr}_{0.97}\text{Mo}_{0.03})_{1-x}\text{Si}_x$  (points with error bars) and of  $\text{Cr}_{1-x}\text{Si}_x$  (points without error bars) with concentration  $x$ . The results for  $\text{Cr}_{1-x}\text{Si}_x$  were taken from Alberts and Lourens (1988). AB represents the ISDW-P transition line for  $\text{Cr}_{1-x}\text{Si}_x$  and BC the CSDW-P line. The broken curve was calculated using equation (2) and separates the ISDW and P states for  $(\text{Cr}_{0.97}\text{Mo}_{0.03})_{1-x}\text{Si}_x$ .

rather flat region of the  $d\rho/dT$  versus  $T$  curve, in the vicinity of  $T_{IC}$ . For other Cr alloys, like Cr-Ge and Cr-Ga (Smit and Alberts 1988), the ISDW-CSDW transition is also characterised by a minimum, which is not as deep as at  $T_N$ , in the  $d\rho/dT$  versus  $T$  curves. In all the  $(\text{Cr}_{0.97}\text{Mo}_{0.03})_{1-x}\text{Si}_x$  samples the flat region with the shallow minimum was

absent in  $d\rho/dT$  versus  $T$  curves between 4 K and  $T_N$  (see figure 1). We conclude from this that the  $(\text{Cr}_{0.97}\text{Mo}_{0.03})_{1-x}\text{Si}_x$  samples do not display ISDW-CSDW transitions and remain in the ISDW state at all temperatures below  $T_N$ . This conclusion was confirmed by preliminary thermal expansion measurements on the samples.

The Néel temperatures of  $(\text{Cr}_{0.97}\text{Mo}_{0.03})_{1-x}\text{Si}_x$  are plotted as a function of  $x$  in figure 3 together with the  $T_N$ -values of Alberts and Lourens (1988) for  $\text{Cr}_{1-x}\text{Si}_x$ . The curve AB separates the ISDW- and P-states of  $\text{Cr}_{1-x}\text{Si}_x$  and the curve BC the CSDW- and P-states. Note that for  $\text{Cr}_{1-x}\text{Si}_x$   $T_N$  increases slightly at first along BC, which is due to the fact that the CSDW phase is more stable than the ISDW phase (Behera and Viswanathan 1969). This type of behaviour is absent in the phase diagram (figure 3) of  $(\text{Cr}_{0.97}\text{Mo}_{0.03})_{1-x}\text{Si}_x$ , confirming the absence of the CSDW phase in this system. The sample with  $x = 0.025$  shows no magnetic anomalies down to 4 K on its  $\rho$ - $T$  curve, implying that anti-ferromagnetism disappears in the  $(\text{Cr}_{0.97}\text{Mo}_{0.03})_{1-x}\text{Si}_x$  system at  $x \approx 0.021$ .

#### 4. Discussion

The main feature of this study is the realisation of a Cr-Mo-Si system in which the CSDW state is completely suppressed. The theory of Dadârlat *et al* (1980) can therefore be applied directly to evaluate the concentration dependence of  $T_N$ . They considered two mechanisms that influence  $T_N$  when a non-magnetic impurity like Si is added to Cr, or in our case to a 'weakened' Cr like  $\text{Cr}_{0.97}\text{Mo}_{0.03}$ . The first of these is a scattering mechanism which causes an electron-hole pair-breaking effect (Zittartz 1967) which always decreases the Néel temperature. The second mechanism is caused by distortions of the Fermi surface when the impurities are added. This mechanism may either increase or decrease  $T_N$  (Crisan and Anghel 1976). Dadârlat *et al* (1980) included both mechanisms to calculate  $T_N$  and obtained

$$\ln(T_N/T_N^0) = \psi(\frac{1}{2}) - \psi(\frac{1}{2} + (\alpha c/T_N)) - [\beta c/(\gamma + c^2)] \quad (1)$$

where  $T_N^0$  is the Néel temperature of the pure system,  $\psi(z)$  is the digamma function,  $c$  is the alloy concentration and  $\alpha$ ,  $\beta$  and  $\gamma$  are fitting parameters. The first two terms together represent the usual pair-breaking effect (Zittartz 1967) and the last term the effect of the change of the density of states on alloying.

Equation (1) may be written (Gradshteyn and Ryzhik 1980)

$$\ln(T_N/T_N^0) = \sum_{k=0}^{\infty} \left( \frac{1}{0.5 + \alpha c/T_N + k} - \frac{1}{0.5 + k} \right) - \frac{\beta c}{\gamma + c^2}. \quad (2)$$

The best fit of equation (2) to the results on  $(\text{Cr}_{0.97}\text{Mo}_{0.03})_{1-x}\text{Si}_x$  (figure 3) is obtained for  $\alpha = 5030$  K,  $\beta = -0.150$  and  $\gamma = 0.00268$ . The fit is shown by the broken curve of figure 3 and is very good. It is rather sensitive to the values of  $\alpha$ ,  $\beta$  and  $\gamma$ . A change of 20 in  $\alpha$ , 0.005 in  $\beta$  or 0.0002 in  $\gamma$  leads to changes in  $T_N$  at  $x = 0.02$  of the order of 100% or more. The value  $\alpha = 5030$  K gives a reciprocal scattering life time of 316 K per 1% Si. In the Cr-Fe system in which Fe forms localised moments, a value of 275 K per 1% Fe is found (Nakanishi and Kasuya 1977).

In conclusion, the addition of Mo to Cr-Si completely suppresses the CSDW phase giving a system that remains in the ISDW phase at all concentrations. The magnetic phase diagram of  $(\text{Cr}_{0.97}\text{Mo}_{0.03})_{1-x}\text{Si}_x$  as determined from electrical resistivity measurements, is well accounted for by the theory of Dadârlat *et al* (1980). Changes in the nesting (the

model assumes perfect nesting) between the electron and hole Fermi surface sheets are not included in their theory. The good fit with experiment may then be taken as evidence that nesting effects are small in  $(\text{Cr}_{0.97}\text{Mo}_{0.03})_{1-x}\text{Si}_x$  alloys and that the main contributions to the decrease of  $T_N$  on alloying result from de-pairing effects caused by impurity scattering and from the changes in the density of states on alloying.

Other theories (Sato and Maki 1974, Antonoff 1977 and Machida and Fujita 1984) that mainly describe changes in  $T_N$  in terms of the effects of imperfect nesting, described by the nesting parameter  $H$  which gives the difference in size between the hole and electron Fermi surface sheets, predict an increase in  $T_N$  when  $H$  is decreased towards zero on alloying. Si acts as an electron donor in Cr (Endoh *et al* 1982) and is expected to decrease  $H$ , thus leading to an increase in  $T_N$  according to the above theories. This is just the opposite of what is observed in the  $(\text{Cr}_{0.97}\text{Mo}_{0.03})_{1-x}\text{Si}_x$  alloys and it is therefore concluded that effects of changes in  $H$  are small compared to the effects of impurity scattering and changes in the density of states on alloying in these alloys.

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