Pressure Dependence of the Magnetic Transition in Cr-Rich Cr-Si Alloys

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The present experimental determination of the pressure dependence of T_N establishes that in Cr-alloys richer than about 1.35 at.% Si, the transition is to a commensurate phase. This can be rationalized only if Si acts as an electron donor to the Cr *d* band and if it goes interstitially into the Cr lattice. The magnetic phase diagram (P-T_N) for Cr-Si alloys has been determined.

We introduce some new ideas to explain the anomalous features of the magnetic transition in Cr-rich silicon alloys. In the absence of neutron diffraction studies, we show by determining the pressure dependence of the antiferromagnetic ordering temperature T_N, that, in Cr-Si alloys containing 1.35 at.% Si and above, the transition is to a commensurate spin density wave (SDW) antiferromagnetic state. Although the electron-to-atom ratio e/a of four for Si is lower than that of Cr, the former has to donate electrons to the *d* band of chromium, in order for the commensurate phase to appear in the Cr-Si alloys. This is possible only when Si goes interstitially into the Cr lattice. To our knowledge this is the first time such a concept has been put forward to explain that an alloyed element with an e/a ratio less than that of Cr can donate electrons and stabilize the commensurate phase.

In dilute *Cr*-Si alloys a sharp first-order transition marked by a discontinuous rise in resistivity[1] and a sharp drop in magnetic susceptibility[2] has been reported. The transition is believed to be due to a change from the paramagnetic to an antiferromagnetically (AF) ordered state (SDW state commensurate with the lattice), but the commensurability has not yet been established by neutron diffraction studies.[3] However, previous studies on Cr-rich alloys with transition metals have shown that the pressure dependence of the Néel temperature, T_N, is a good indicator in classifying the nature of the magnetically ordered phase.[4] Therefore, in the present study, the shift in the Néel temperature with pressure in Cr-rich Si alloys over the range of composition from 0.9 to 2.74 at.% Si has been determined.

The sample preparation methods, the experimental techniques for measuring the resistivity,[1] and the hydrostatic pressure generation[5] techniques have been described previously.

In the inset of Fig. 1 the observed resistance anomalies at different pressures for a *Cr*-Si alloy containing 1.85 at.% Si are shown. At higher pressures the resistance anomaly loses its sharpness and appears to be much smaller. The transition temperatures are plotted in Fig. 1 as a function of pressure, P, for some of the samples studied. Only in the sample containing 0.9 at.% Si is the slope dT_N/dP close to the value normally observed for the paramagnetic to the incommensurate transition.[4] For *Cr*-Si alloys with

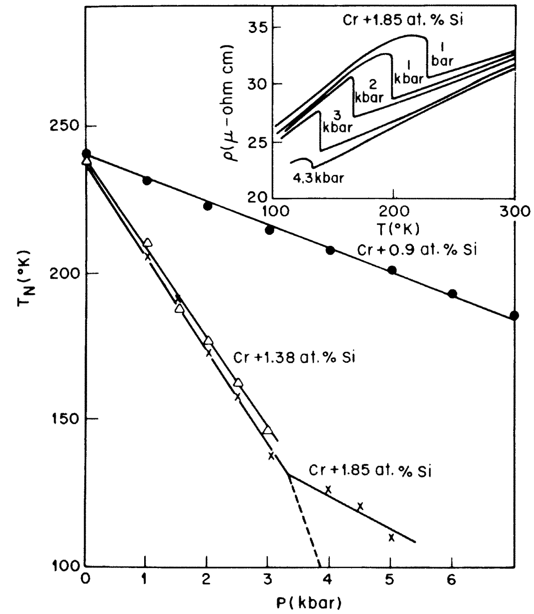

FIG. 1. Pressure dependence of the Néel temperature for *Cr*-Si alloys. The inset shows the sharp, abrupt nature of the resistance anomaly associated with the transition.

1.38 at.% Si and 1.85 at.% Si the slopes are almost identical and have the value of about 30°K/kbar. Between 3 and 4 kbar pressures dT_N/dP appears to decrease abruptly to a value closer to that of Cr with 0.9 at.% Si. In the Cr-2.74 at.% Si sample a sharp resistance anomaly is seen but dT_N/dP is found to be about 25°K/bar.

Previous studies on Cr-rich alloys containing transition metal additions such as Mn and Ru have shown that dT_N/dP for the paramagnetic to the commensurate AF phase boundary is much larger compared to the paramagnetic to the incommensurate AF phase boundary, i.e., 15–20°K/kbar versus 6°K/kbar.[4] Also, in Cr-rich Fe alloys containing more than 2 at.% Fe a sharp discontinuous rise in resistivity similar in character to that of *Cr*-Si alloys has been observed.[6] Neutron diffraction studies on *Cr*-Fe alloys have shown that this transition is from the incommensurate AF to the commensurate AF phase.[7] Furthermore, the pressure dependence of this transition is found to be larger, i.e., $dT_N/dP \simeq 22$°K/kbar.[8,9] Comparing the results of the present study on *Cr*-Si alloys with results mentioned above we conclude that the sharp and large resistance anomaly in the latter is due to a transition to the commensurate AF phase. We attribute the break in the slope in Fig. 1 for the 1.85 at.% Si alloy to a change in the transition from the paramagnetic to the incommensurate AF phase. The magnetic $P - T_N$ diagram for the 1.85 at.% Si alloy must have a triple point at about 4 kbar and at about 130°K. We lack experimental data on the commensurate-incommensurate phase boundary, but the dashed line indicates its probable location.

Neutron diffraction studies on Cr alloys containing several transition metal additions have established that the commensurate-incommensurate SDW structure of the AF state can exist, depending on whether the e/a ratio of six for Cr is increased or decreased by the addition of other elements.[4] Thus metals such as Mn, Ru, and Os whose e/a ratios are greater than that of Cr raise the T_N of the SDW state of Cr and stabilize the commensurate phase at an e/a slightly greater than six, while addition of *V* with e/a of five rapidly depresses the T_N of the incommensurate SDW state. Pressure always acts in the direction of decreasing e/a. If the e/a criterion is valid, the commensurate AF phase would be ruled out for Si addition, since the e/a for Si is four. Thus the appearance of a commensurate AF phase in *Cr*-Si alloys is in apparent contradiction to the expectation from the e/a agrument. But, it is a firmly established fact that the commensurate phase cannot occur unless there is a donation of electrons to the *d* band of Cr and the electron Fermi surface enlarges in relation to the hole surface. This leads to two conclusions: (i) That Si must act as an electron donor when introduced into Cr and that the addition of Si to Cr effectively increases the e/a ratio. The magnetic susceptibility measurements on *Cr*-Si alloys appear to support this argument since the paramagnetic susceptibility decreases with increasing Si concentration. (ii) That Si goes into Cr interstitially, prompting the Si to act as an electron donor to the *d* band of Cr. We believe that if Si went in substitutionally, the valence electrons of Si would be constrained to participate in the covalent bonding with the neighboring Cr; and thus the Si would not be free to donate the electrons. There should be no such constraint, if on the other hand Si went in interstitially into the chromium lattice. Thus we arrive at the interesting result that the e/a ratio would also depend upon whether the added element enters the Cr lattice substitutionally or interstitially.[10]

The large negative value for the dT_N/dP[8,9] for for the phase boundary indicates an anomalously large thermal expansion in the first-order transition to the commensurate phase in *Cr*-Si alloys. This expansion is comparable to that observed in *Cr*-Fe alloys. From the measured thermal expansion $\Delta V/V$ of 0.124%[11] and dT_N/dP of ~30°K/kbar, we estimate, using the Clausius-Clapeyron equation $dT/dP = \Delta V/\Delta S$, the entropy change ΔS to be 0.007 cal/mole K. The entropy change at the magnetic transition for Cr-3 at.% Fe alloy of about 0.01 cal/mole K compares favorably with the value for the *Cr*-Si alloy. Ishikawa, Hoshino, and Endoh[6] have argued that the large thermal expansion at the transition in *Cr*-Fe alloy is due to the gain in the magnetic energy realizable through expansion in the commensurate phase compared to the elastic energy. The larger expansion results in an increase in the interaction area between the electron and the hole Fermi surface and hence further lowers the magnetic energy. In addition to the ideas described above, this mechanism may also be relevant to the *Cr*-Si alloys. The pressure dependence of T_N is certainly consistent with the anomalously large expansion in the commensurate AF phase of *Cr*-Si alloys in that it is found to be much larger than in any other Cr-rich alloys studied so far. A neutron diffraction study of Cr-Si alloys would be of great interest and it is hoped that this Letter will stimulate such a study.

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[11] Private communication: Professor O. Beckman, University of Uppsala, Uppsala, Sweden.

Electronic Structure of Stacking Faults in Transition Metals: Nickel

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We report the results of a calculation which point out the existence of localized electronic states in the vicinity of stacking faults in a face-centered-cubic transition metal (nickel). The results are fairly insensitive to the parameters of the calculation. The reported states appear between the two *d* sub-bands of the bulk states, are well received, are fairly well localized, and could be observable by electron emission spectroscopy.

Although stacking faults in close-packed metals are one of the better known and more extensively studied defects from the point of view of structural properties,[1-3] the electronic properties of such faults have not been examined in any detail.[4] This is due to two causes: (a) The fault is not a point defect and yet it destroys the periodicity of the crystal in one of the three dimensiones; and (b) the experimental studies of the electronic properties of crystals have not yet achieved enough resolution to detect features related to a fault. Both these drawbacks are now in the process of being removed. The progress achieved in the last few years in studying theoretically the electronic properties of surfaces[5-10] and interfaces[9] by a variety of methods makes it possible to extend such studies in a straightforward way to a planar defect. In addition, the accuracy and sophistication of the various experimental methods designed to study electronic properties of surfaces and interfaces,[11] including the various photoemission spectroscopies,[12] make it evident that reliable data on the electronic properties of stacking faults should be forthcoming in the near future.

The structural properties of the stacking faults in face-centered-cubic metals are reasonably well known.[1,13,14] The energy of formation of such a fault in pure nickel has been quoted to be as low[15] as 80–100 erg/cm^2 and as high[14] as 300 erg/cm^2. In any case, these energies guarantee that enough of them can be obtained under ordinary but controlled conditions to insure accurate measurements.

We have studied the electronic properties of both the intrinsic and extrinsic stacking faults[1] in face-centered-cubic nickel using a transfer-matrix method previously developed for surfaces.[10,16] We have used a basis set of six functions per atom (one *s* function and five *d* functions) with the parameters obtained from previous calculations[5] and from proper fitting to established band structures.[17] Our parameters are, in the notation of Slater and Koster[18] (in eV),

$$s_0 = 5.000, \quad d_0 = 0,$$

$$(ss\sigma) = -1.000, \quad (sd\sigma) = -0.748,$$

$$(dd\sigma) = -0.567, \quad (dd\pi) = +0.256,$$

$$(dd\delta) = -0.032.$$