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ABSTRACT

From the pressure dependence of the Néel temperature (T_N) in Cr-Ge alloys, the AF transition is found to be to the commensurate state, when Ge > 0.6 at.%. Our EXAFS study on Cr-Ge shows clearly that Ge goes substitutionally into the Cr lattice. These findings raise the interesting question why Si and Ge additions stabilize the commensurate phase, despite their smaller e/a ratio.

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From the pressure dependence of the Néel temperature (T_N) of Cr-Si alloys it has been shown[1] that the commensurate spin density wave state (CSDW) becomes stable in alloys with more than about 1.35 at.% Si. The stabilization of the commensurate phase for Si addition violates the e/a ratio rule.[2] In this connection Jayaraman et al.[1] suggested that Si could go interstitially into the Cr lattice and act as an electron donor. In the present investigation we have studied Cr-Ge alloys, because they undergo commensurate ordering and at the same time are amenable to an EXAFS study to ascertain the position of Ge in the Cr-lattice. Such a study was not possible with Cr-Si due to the limitation of EXAFS to elements with $Z > 25$. To our knowledge this is the first application of EXAFS to this field. The results are presented and discussed.

Arajs and Katzenmeyer[3] first investigated the electrical resistivity of Cr-Ge alloys, but did not report a transition to the CSDW state. In a later study Suzuki[4] carried out thermal expansion measurements on Cr-Ge alloys and found the existence of the CSDW state, at Ge concentrations $\geqslant 0.32$ at.%. More recently Arajs et al.[5] have found a resistance anomaly corresponding to this transition. Also a recent neutron diffraction study[6] has confirmed the CSDW phase.

The experimental techniques including the sample preparation are described elsewhere.[7] In the inset of Fig. 1 the observed resistance anomalies at different pressures for a Cr-Ge alloy containing 1.0 at.% Ge are shown. The resistance anomaly is not as sharp as in the case of Cr-Si alloys. Scanning electron microscope (SEM) studies revealed that the sharpness of the resistance anomaly is connected with the homogeneity of the sample. Using SEM, we excluded those samples which showed inhomogeneous regions (within the μm-resolution of the SEM). The transition temperatures determined from the minima in the resistance-temperature curves at constant pressure are plotted in Fig. 1 as a function of pressure. Only in the sample containing 0.4 at.% Ge is the slope $dT_N/dP \approx -6.4$°/kbar close to the value normally observed for the paramagnetic (P) to the incommensurate (I) transition[2]. In the case of Cr-Ge alloys with 0.6 at.% Ge and 1.0 at.% Ge the slopes are ~ -30°/kbar and ~ -20°/kbar, respectively. For Cr + 0.6 at.% Ge the slope changes abruptly to about -7.6°/kbar near 2 kbar and for Cr + 1.0 at.% Ge to about -10.5°/kbar near 6 kbar. Following the earlier study[1], we identify the phase boundary having the larger slope with the transition from paramagnetic (P) to the commensurate (C) AF-state, and the break in the slope in Fig. 1 for the 0.6 at.% Ge and 1.0 at.% Ge alloy to a change in the transition from (P) to the (I) AF-state. The magnetic phase diagram for Cr-Ge alloys richer than 0.6 at.% Ge must have a triple point. The C-I phase boundary could not be determined from resistivity measurements for the reason that no resistance anomaly is observable even at atmospheric pressure, although such a transition is known to be present from other measurements. For instance no resistance anomaly is seen corresponding to the C-I transition reported in Cr + 0.6 at.% Ge alloy at about 220 K from thermal expansion measurements[4].

According to the rigid-band model for Cr-alloys[2] the commensurate phase cannot occur, unless there is a donation of electrons to the d-band of Cr. Evidently this is satisfied with transition metals having an e/a ratio greater than 6. However in the case of Si and Ge with an e/a of 4, donation of electrons is hard to understand. To rationalize the behavior of Cr-Si alloys Jayaraman et al.[1] suggested that Si possibly goes into Cr interstitially, in which case there should not be any structural constraint on Si to act as an electron donor to the d-band of Cr. Fortunately the Cr-Ge alloys are suited for an EXAFS-study to settle the question[8]. We have therefore carried out EXAFS measurements on Cr + 1.0 at.% Ge with the spectrometer ROEMO at the Hamburger Synchrotronstrahlungslabor HASYLAB DESY (Hamburg).

The theory of EXAFS and the EXAFS analysis is described elsewhere[9]. Fig. 2a shows the EXAFS spectra obtained from the data measured at the K edges of Cr and Ge in pure *Cr* and in the Cr + 1.0 at.% *Ge* alloy, after background removal[10]. In Fig. 2b the Fourier transform (FT) of the EXAFS data are displayed, which is related to the radial distribution function for the neighbour shells[9]. Both EXAFS FTs have been obtained using the same k-value range from $3.5 - 11.5$ Å^{-1} and a k-weighted Gaussian window[10]. To remove the influence of the scattering phase, which is different for the Cr-Cr and Ge-Cr pairs, the phases calculated by Teo and Lee[11] have been used for the transformation. Therefore the two FTs are comparable and the maxima of those EXAFS FTs are at the real distances as indicated by arrows for the case of pure Cr. For completeness we also give the coordination numbers and the distances of the nearest neighbour shells in pure Cr, determined from X-ray diffraction data[12]. If one neglects the differences of the heights, both EXAFS FTs look nearly the same. This indicates clearly that the Ge-atom in the Cr + 1.0 at.% Ge alloy has the same surrounding of Cr-atoms as the Cr-atom in pure Cr. In other words: the Ge-atom goes substitutionally into the Cr lattice.

Furthermore the heights of the peaks corresponding to the shells from the third to the sixth one in both FTs can be made equal by scaling the FT of Cr + 1.0 at.% Ge by a factor of 0.73. This increase of the EXAFS amplitude in the case of the central Ge-atom in the Cr-Ge alloy seems to indicate a decrease of damping of the outgoing photoelectron compared with the case of the central Cr-atom. This may be a hint that the Ge-atom is not bound metallic. After scaling, differences in the EXAFS FTs are obvious in the range from 1.5 to 3.6 Å. The peak in this range corresponds to scattering atoms in the first and second shell, which are close together ($\Delta R = 0.386$ Å in pure Cr). This range of the FTs is back transformed[10] to k-space. The results are shown in Fig. 2c as circles. Fitting these curves by a two shell EXAFS model with distances mean square displacement and coordination numbers as parameters, and using the backscattering amplitudes of Cr calculated by Teo et at.[13] we have obtained the solid lines in Fig. 2c. The fits yield the result that the second shell of Cr-atoms surrounding the Ge-atom in the Cr-Ge alloy has the same distance, but the first shell is displaced by 5/100 Å to a larger value compared with the case of pure Cr. Further the numbers of nearest neighbours are the same as in pure Cr, 8±1 in the first and 6±1 in the second shell.

Finally we want to point out two more facts which support our result that Ge goes substitutionally into the Cr lattice. Characteristic of the bcc structure is the anomalous strong peak (at 5.8 Å in the Cr FT) corresponding to the sixth-nearest neighbour shell. This is a result of forward scattering[9] of the outgoing electron wave by the atoms of the second shell, which are directly in line with the atoms of the sixth-nearest neighbour shell. Especially the fact that this peak is still strong in the Cr + 1.0 at.% Ge alloy provides strong evidence that not only the long-range coherence is maintained out to the latter shell, but also that the displacement vectors of the Cr-atoms from the Ge central scattering atom are radial. Marcus[14] has pointed out that interstitial atoms would show up in FT plots of the data as a peak at low distances or as a beatnote in the data in k-space[15]. Both features cannot be found in our case.

In summary, we have confirmed the existence of the CSDW state in Cr-Ge alloys with a Ge concentration ⩾ 0.4 at.%. Our EXAFS-study clearly indicates that Ge goes substitutionally into the Cr lattice. From this we can also state that Si in Cr-Si is not interstitial but substitutional[16]. Thus we are back to the question how an added element with e/a ratio of less than 6 can stabilize the CSDW state in Cr-Si and Cr-Ge alloys. The hint that the Ge is not metallically bound in the Cr lattice, a fact which may also be reflected in the XANES (X-ray near Edge Structure), may be the clue. Instead of enlarging the electron Fermi surface the addition of Cr or Si may have the effect of reducing the hole Fermi surface of Cr, which can also lead to better matching of the electron and hole Fermi surfaces, resulting in the commensurate SDW state.

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Figure Captions

Fig. 1 Pressure dependence of the Néel temperature for Cr-Ge alloys. the solid line has been drawn connecting the data points. The inset shows the resistance anomaly associated with the transition.

Fig. 2 a) EXAFS of CR + 1.0 at.% Ge and Cr. The data were taken with use of the Ge K edge and of the Cr K edge, respectively.

b) Fourier transforms of the EXAFS data for Cr + 1.0 at.% Ge and pure Cr. The EXAFS FTs have been obtained using the same k-value range from 3.5 – 11.5 Å^{-1} and a k-weighted Gaussian window for the transformations and taking into account the difference in the scattering phase of Cr-Ge and Cr-Cr pairs.

c) The EXAFS spectra back transformed from the EXAFS FTs in the range from 1.5 – 3.6 Å (indicated by circles). Solid lines: Two shell fits with distances, mean square displacement and coordination numbers as parameters and the theoretical backscattering amplitude of Cr[13].

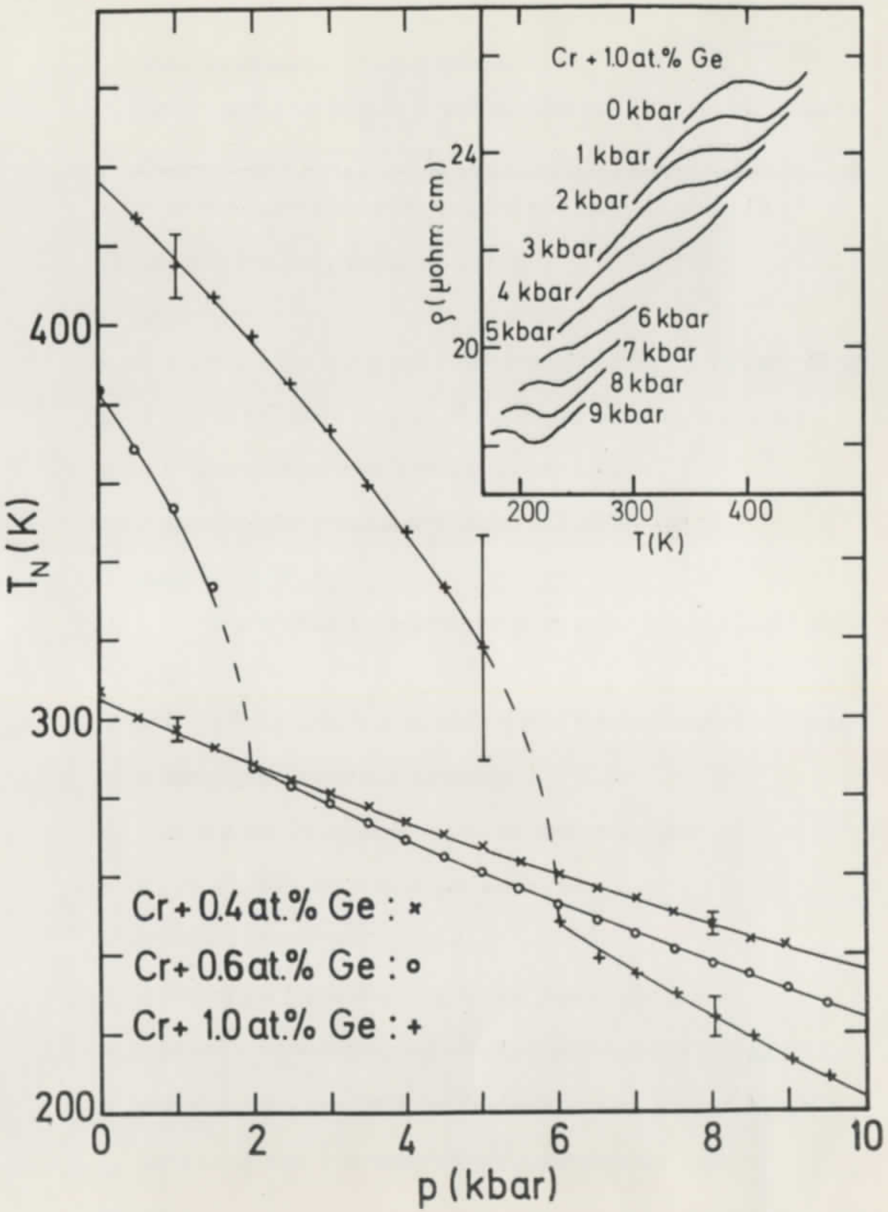

Fig. 1

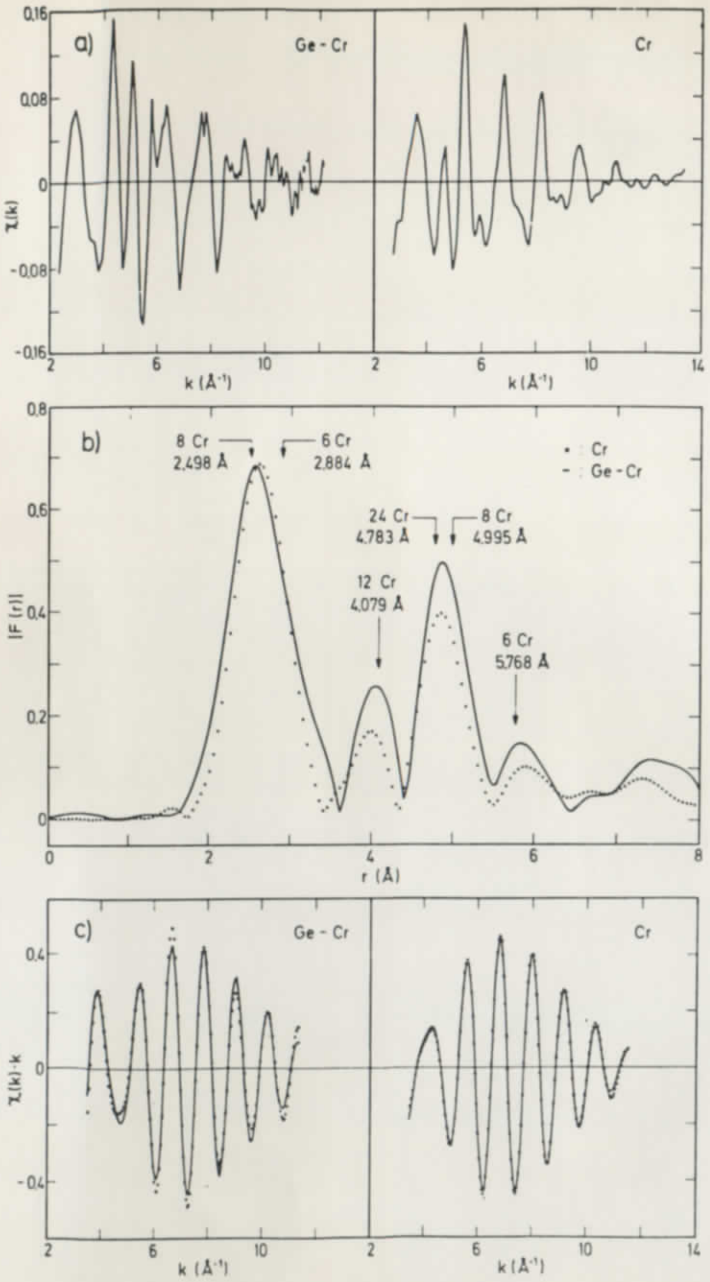
a)
Ge - Cr
Cr
0,16
0,08
0
-0,08
-0,16
χ(k)
2
6
10
14
k (Å⁻¹)
b)
8 Cr
2,498 Å
6 Cr
2,884 Å
• : Cr
- : Ge - Cr
24 Cr
4,783 Å
8 Cr
4,995 Å
12 Cr
4,079 Å
6 Cr
5,768 Å
0,8
0,6
0,4
0,2
0
|F(r)|
0
2
4
6
8
r (Å)
c)
Ge - Cr
Cr
0,4
0
-0,4
χ(k)·k
2
6
10
14
k (Å⁻¹)

Fig. 2