High-Pressure and Extended X-Ray-Absorption Fine-Structure Study of Cr-Rich Cr-Ge Alloys

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From the pressure dependence of the Néel temperature (T_N) in Cr-Ge alloys, the anti-ferromagnetic transition is found to be to the commensurate state, when Ge is greater than 0.6 at.%. The present extended x-ray-absorption fine-structure study on Cr-Ge shows clearly that Ge goes substitutionally into the Cr lattice. On the basis of the rigid-band model this can be understood only if Ge acts as an electron donor to the d band of Cr. These findings raise the interesting question as to how Si and Ge additions stabilize the commensurate phase, despite their smaller e/a ratio.

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 (CSDW) state 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 extended x-ray-absorption fine-structure (EXAFS) study to ascertain the position of Ge in the Cr lattice. Such a study was not possible with Cr-Si because of the limitation of EXAFS to elements with $Z \geqslant 25$. 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, Aidun, and Moyer[5] have found a resistance anomaly corresponding to this transition. Also a recent neutron diffrac-

tion 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 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 micrometer 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 $dT_N/dP = -6.4°/$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 $\approx -30°/$kbar and $\sim -20°/$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 the paramagnetic
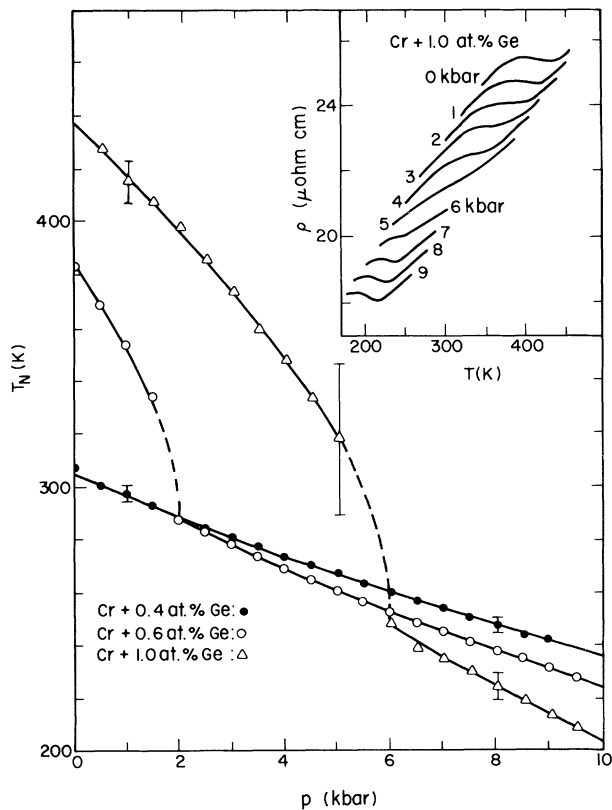
FIG. 1. Pressure dependence of the Néel temperature for Cr-Ge alloys. The solid line has been drawn connecting the data points. The inset shows the resistance anomaly associated with the transition.

(P) to the commensurate (C) antiferromagnetic (AF) state, and the break in the slope in Fig. 1 for the 0.6-at.%-Ge and 1.0-at.%-Ge alloys to a change in the nature of the transition from P to 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]

Neutron diffraction studies on Cr alloys containing transition-metal additions have shown[2] that the existence of the C or I SDW state in Cr alloys depends sensitively on the e/a ratio. If the added element has a e/a ratio greater than 6 the commensurate state becomes stable, and if it is less than 6 the incommensurate state is fav-

ored. This criterion suggests that the addition of Si, Ge, or Sn should not result in the formation of the CSDW state, since the e/a ratio for all these elements is only 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 explain the behavior of Cr-Si alloys Jayaraman et al.[1] suggested that Si may go into Cr interstitially, in which case there should not be any structural constraint on Si to prevent it from acting as an electron donor to the d band of Cr. Fortunately the Cr-Ge alloys are suitable for an EXAFS study to settle the question of whether Ge goes substitutionally or interstitially into the Cr lattice.[8] We have therefore carried out EXAFS measurements on Cr + 1.0 at.% Ge with the spectrometer ROE MO at the Hamburger Synchrotronstrahlungslabor (HASYLAB) at Deutsches Elektronen-Synchrotron (DESY) in Hamburg.

The theory of EXAFS and its analysis are described elsewhere.[9] Figure 2(a) 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. 2(b) the Fourier transform (FT) of the EXAFS data which is related to the radial distribution function for the neighbor shells is displayed.[9] Both EXAFS FT's have been obtained with the same k-value range from 3.5 to 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 FT's are comparable and the maxima of those EXAFS FT's 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-neighbor shells in pure Cr, as determined from x-ray diffraction data.[12] If one neglects the differences in the heights, both EXAFS FT's 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 in both FT's can be made equal by scaling the FT
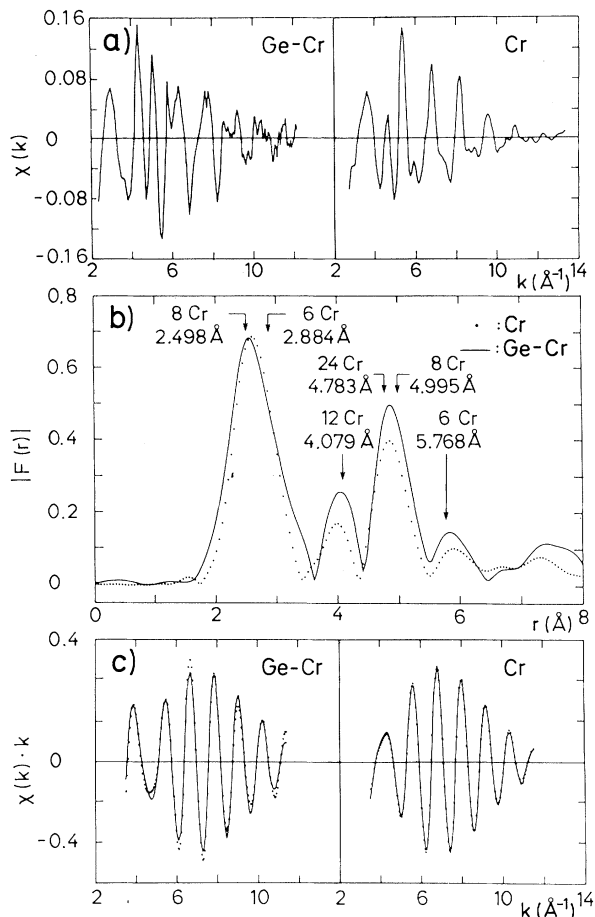
FIG. 2.   (a) EXAFS of Cr + 1.0 at.% Ge and pure Cr.
The data were taken with use of the Ge K edge and of
the Cr K edge, respectively. (b) Fourier transforms
of the EXAFS data for Cr + 1.0 at.% Ge and pure Cr.
The EXAFS FT's have been obtained with use of the
same k value range from 3.5 to 11.5 Å^{-1} and a k-
weighted Gaussian window for the transformations and
with account taken of the difference in the scattering
phases of Cr-Ge and Cr-Cr pairs. (c) The EXAFS
spectra back transformed from the EXAFS FT's in the
range from 1.5 to 3.6 Å (indicated by circles). Solid
lines: Two-shell fits with distances, mean square dis-
placement, and coordination numbers as parameters
and the theoretical backscattering amplitude of Cr (Ref.
13).

of Cr + 1.0 at.% Ge by a factor of 0.73. This in-
crease of the EXAFS amplitude in the case of the
central Ge atom in the Cr-Ge alloy seems to in-
dicate a decrease of damping of the outgoing pho-
toelectron as compared with the case of the cen-
tral Cr atom. This may be a hint that the Ge
atom is not bound metallically. After scaling,
differences in the EXAFS FT's 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 (ΔR
= 0.386 Å in pure Cr). This range of the FT's is
back transformed[10] to k space. The results are
shown in Fig. 2(c) as circles. Fitting these
curves by a two-shell EXAFS model with distanc-
es, mean square displacement, and coordination
numbers as parameters, and using the backscat-
tering amplitudes of Cr calculated by Teo et al.,[13]
we have obtained the solid lines in Fig. 2(c). The
fits yield the result that the second shell of Cr
atoms surrounding the Ge atom in the Cr-Ge al-
loy is at the same distance as in pure Cr, but the
first shell is displaced by 5/100 Å to a larger
value as compared with the case of pure Cr. Fur-
thermore, the numbers of nearest neighbors are
the same as in pure Cr, 8± 1 in the first and 6
± 1 in the second shell.

Finally we wish to point out two more facts
which support our contention that Ge goes sub-
stitutionally into the Cr lattice. A characteristic
of the bcc structure is the anomalous strong peak
(at 5.8 Å in the Cr FT), corresponding to the
sixth-nearest-neighbor shell. This is a result of
forward scattering[9] of the outgoing electron wave
by the atoms of the second shell, which are di-
rectly in line with the atoms of the sixth-nearest-
neighbor shell. The fact that this peak is still
strong in the Cr + 1.0 at.% Ge alloy provides es-
pecially strong evidence that not only is the long-
range coherence 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 beat note in the da-
ta 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 con-
centration ≥ 0.4 at.% Our EXAFS study clearly in-
dicates 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 must return to the question of how an added
element with e/a ratio of less than 6 can stabi-
lize 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 x ray near-edge structure, may be the clue.
Instead of enlarging the electron Fermi surface
the addition of Ge or Si may have the effect of re-
ducing 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.

We would like to thank the HASYLAB staff for help in running the experiment and Dr. B. Lengeler for helpful discussions.

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