

## Antiferromagnetism and electrical resistivity of dilute chromium-germanium alloys

Sigurds Arajs, R. Aidun, and C. A. Moyer

Department of Physics, Clarkson College of Technology, Potsdam, New York 13676

(Received 7 May 1980)

Electrical resistivity from 4 to 700 K is reported for dilute Cr alloys containing 0.35, 1.1, 1.4, and 2.2 at. % Ge. The implications of this study for the magnetic phase diagram of Cr-Ge alloys are compared with recent results from thermal expansion measurements by Suzuki, and agree with the existence of a magnetic triple point at  $\sim 0.35$  at. % Ge. Contrary to the rigid-band hypothesis, Ge acts as an electron donor when substituted into the Cr matrix. We argue that this puzzling result can be understood in terms of virtual impurity levels lying above the Fermi level of Cr. Identical considerations are shown to hold for Si impurities in Cr, and may account for the anomalous residual resistance and pronounced resistivity enhancements seen at the Néel temperatures of these alloys.

### I. INTRODUCTION

Below the Néel temperature  $T_N = 312$  K, chromium is an itinerant electron antiferromagnet possessing a spin-density-wave (SDW) structure which is incommensurate ( $I$ ) with the lattice. Above  $T_N$  chromium is paramagnetic ( $P$ ). When other elements are dissolved in chromium,  $T_N$  can monotonically increase, decrease, or oscillate with respect to the solute concentration.<sup>1</sup> According to our earlier study<sup>2</sup> of the electrical resistivity,  $\rho$ , of dilute chromium-germanium alloys between 4 and 320 K,  $T_N$  decreases with increasing germanium content. However, a recent investigation of the thermal expansion by Suzuki<sup>3</sup> on dilute chromium-germanium alloys up to 500 K indicates that the magnetic phase diagram of this system is more complicated than originally suspected. Specifically, Suzuki suggests the existence of a magnetic triple point at 0.32 at. % Ge where the paramagnetic ( $P$ ), incommensurate ( $I$ ), and commensurate ( $C$ ) phase boundaries meet. Because of these findings, we decided to extend our electrical resistivity studies on the chromium-germanium system to temperatures above 300 K. The results of these studies and their significance are briefly described in this paper.

### II. EXPERIMENTAL CONSIDERATIONS

The chromium-germanium alloys containing 0.35, 1.1, 1.4, and 2.2 at. % Ge are the same as those used before.<sup>2</sup> Reference 2 gives preparation details and purity characterizations.

The electrical resistivity measurements above room temperature were made using the four-probe technique described elsewhere.<sup>4</sup>

### III. RESULTS AND DISCUSSION

Figure 1 shows the electrical resistivity of chromium-germanium alloys containing 0.35, 1.1, 1.4, and 2.2 at. % Ge as a function of temperature ( $T$ ) between 4 and 700 K. The  $\rho$  vs  $T$  curves below 300 K were constructed using data obtained in our earlier study.<sup>2</sup> As the figure clearly indicates, the curves for 1.1, 1.4, and 2.2 at. % Ge exhibit well-defined anomalies characteristic of the Néel transition. It is now well-known that  $T_N$  of chromium systems can be easily determined from plots of the temperature coefficient of electrical resistivity,  $(1/\rho)(d\rho/dt)$ , as a function of temperature. Specifically,  $T_N$  is the temperature at which  $(1/\rho)(d\rho/dt)$  exhibits a sharp minimum. Figure 2 shows such plots, obtained by numerical differentiation of the resistivity data in Fig. 1. We find from Fig. 2 that the values of  $T_N$  for 0.35, 1.1, 1.4, and 2.2 at. % Ge samples are, respectively,  $300 \pm 5$ ,  $420 \pm 2$ ,  $430 \pm 2$ ,

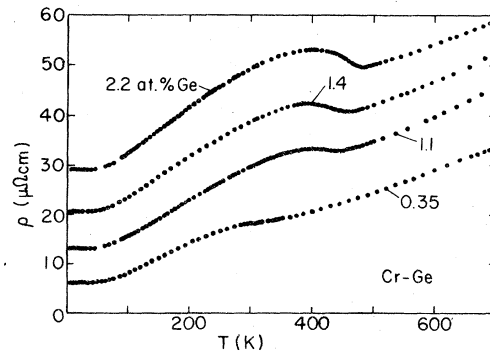


FIG. 1. Electrical resistivity of dilute chromium-germanium alloys between 4 and 700 K.

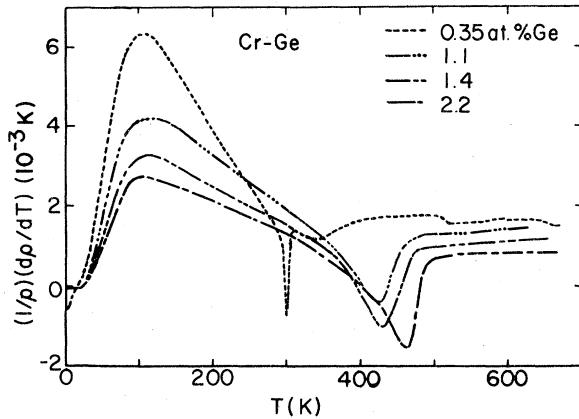


FIG. 2. Temperature coefficient of the electrical resistivity of dilute chromium-germanium alloys between 4 and 700 K.

and  $461 \pm 2$  K. This information is presented in Fig. 3, which shows the magnetic phase diagram of the chromium-germanium system. Also shown in this figure are points calculated from Fig. 3 of Ref. 3 and a point from our earlier investigation.<sup>2</sup>

The results of the present study are fully consistent with Suzuki's thermal-expansion investigations. In particular, we agree with the existence of a triple point near 0.35 at. % Ge concentration. The small  $\rho$  anomaly in the 0.7 at. % Ge sample which we previously reported<sup>2</sup> as  $T_N$  is actually the transition temperature separating the commensurate (C) and incommensurate (I) phases. In summary, we see that

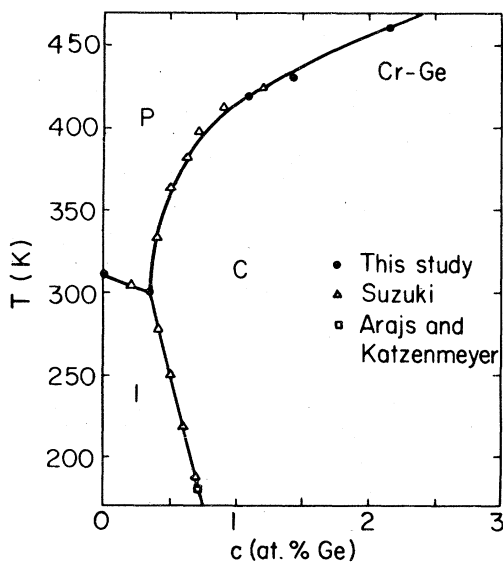


FIG. 3. Magnetic phase diagram of dilute chromium-germanium alloys.

small (less than 0.35 at. %) additions of germanium to chromium decrease  $T_N$  by  $\sim 34$  K/at. % Ge. Above 0.35 at. % Ge the spin-density wave becomes commensurate with the lattice, and  $T_N$  increase rapidly with increasing germanium content.

It is now generally accepted that the itinerant antiferromagnetism in chromium results from the pairing of opposite-spin electrons on the Fermi surface whose wave vectors differ by  $Q$ , the spin-density wave vector. The initial decrease in  $T_N$  and the magnetic behavior at the triple point suggest the existence of a depairing mechanism which operates in the incommensurate phase below 0.35 at. % Ge, but is neutralized with the onset of commensurate ordering. Such a mechanism must originate in harmonics of the fundamental SDW, which then disappear in the commensurate phase. The most likely source is the second harmonic charge-density wave (CDW) with its accompanying strain wave (SW). In particular, we note that a periodic displacement of the lattice ions might result in a measurable depairing effect, especially in the light of the rapid decrease in  $T_N$  observed in chromium with the application of hydrostatic pressure.<sup>5</sup>

The switch to commensurate ordering at 0.35 at. % Ge and consequent rapid increase in  $T_N$  indicates that the germanium impurities donate electrons to the chromium host, in violation of the rigid-band hypothesis. Thus, the replacement of a chromium atom, having six valence electrons, with a germanium atom having only four ought to result in a net deficiency of two electrons per impurity. But this argument overlooks the effect of impurities on the host band structure which, *de facto*, must be important in the chromium-germanium system. In particular, alloying alters the host density of states

$$N(E) \rightarrow N(E) + \delta N(E) \quad (1)$$

and this, in turn, shifts the Fermi level, giving rise to an "apparent" electron atom ratio different from the "bare" result of rigid-band theory.

To make this idea quantitative, we appeal to a little-used formula of scattering theory. In the present case, band electrons scatter from germanium impurities embedded in the chromium host. If multiple scattering can be ignored (dilute alloys), the correction to the density of states per atom  $\delta N(E)$  is<sup>6,7</sup>

$$\delta N(E) = \frac{c}{2\pi i} \frac{d}{dE} \text{Tr} \ln S(E) \quad (2)$$

where  $c$  is the atomic fraction of solute and  $S(E)$  the  $S$  matrix for a single scatterer. The Fermi energy  $E_F$  relative to that of pure chromium  $E_F^0$  is given by

$$\delta n c = \int_{E_F^0}^{E_F} [N(E) + \delta N(E)] dE \quad (3)$$

where  $\delta n$  is the impurity valence relative to chromi-

um ( $\delta n = -2$  for Ge in Cr). But the second term on the right is proportional to solute concentration and, thus, can be absorbed into  $\delta n$  to give an apparent number of electrons per impurity  $\delta n_s$  donated to the host bands

$$\delta n_s = \delta n - (1/2\pi i) \text{Tr} \ln S(E_F) . \quad (4)$$

Equation (4) is the sought-after result; its interpretation is facilitated if we imagine the chromium ions to be smeared out into a uniform background of positive charge (jellium) surrounding the impurity scatters. For spherically symmetric scattering the eigenvalues of  $S(E_F)$  are  $\exp[2i\eta_l(E_F)]$ , where the  $\eta_l$  are the scattering phase shifts, and there results

$$\delta n_s = \delta n - \frac{1}{\pi} \sum_0^{\infty} 2(2l+1)\eta_l(E_F) . \quad (5)$$

For germanium in chromium the scattering potential is repulsive (corresponding to a net ionic charge of  $+4e - 6e = 2e$ ), thus  $\eta_l$  is negative and  $\delta n_s > \delta n = -2$ ; i.e., the residual impurity charge of  $-2e$  is *screened* by holes in the host conduction band according to Eq. (5). For total screening we set  $\delta n_s = 0$  and recover the *Friedel sum rule*<sup>8</sup>

$$\delta n = \frac{1}{\pi} \sum_0^{\infty} 2(2l+1)\eta_l(E_F) . \quad (6)$$

But the degree of screening cannot be known *a priori*; indeed, germanium in chromium appears to be an electron donor; i.e.,  $\delta n_s > 0$ , as if the screening were *more than total*. Such intriguing behavior is not

forbidden by Eq. (5) and, indeed, is expected if the scattering potential were strong enough to introduce a virtual level into the spectrum above  $E_F$ , or actually split off a bound state from the top of the band. Either way the density of *occupied* levels would have to be reduced to keep the total number of band states fixed: more precisely, we must have

$$\int \delta N(E) dE = 0 , \quad (7)$$

with the result that the Fermi level would rise, *as if* electrons were being donated to the band. Similar arguments have been invoked previously to explain the magnetic behavior of nickel containing small amounts of dissolved silicon.<sup>9</sup> It is not surprising then that this mechanism also applies to chromium containing germanium. Indeed, the same conclusions ought to hold for the chromium-silicon system. In this connection, we note that the magnetic phase diagram for Cr-Si (Ref. 10) is tantalizingly similar to our Fig. 3, but with a triple point at  $\sim 1.0$  at. % Si followed by only a barely discernible rise in  $T_N$ . Apparently, silicon too acts as a donor in chromium, but much less so than germanium, as might be expected if the virtual level in Cr-Si was formed closer to the Fermi surface. This is reasonable since silicon, with its smaller ionic core, should bind electrons more tightly than germanium. Moreover, the appearance of virtual levels near the Fermi surface would account for the anomalous residual resistance observed in Cr-Ge and Cr-Si alloys, as well as the pronounced resistivity enhancements seen at the Néel temperature.<sup>11</sup>

<sup>1</sup>S. Arajs, K. V. Rao, H. U. Åström, and T. F. DeYoung, Phys. Scr. **8**, 109 (1973).

<sup>2</sup>S. Arajs and W. E. Katzenmeyer, J. Phys. Chem. Solids **28**, 1459 (1967).

<sup>3</sup>T. Suzuki, J. Phys. Soc. Jpn. **45**, 1852 (1978).

<sup>4</sup>S. Arajs, R. H. Flora, and E. E. Anderson, J. Nucl. Mater. **37**, 89 (1970).

<sup>5</sup>D. B. McWhan and T. M. Rice, Phys. Rev. Lett. **19**, 846 (1967).

<sup>6</sup>F. Gautier, Z. Angew. Phys. **24**, 289 (1968).

<sup>7</sup>J. S. Langer and V. Ambegaokar, Phys. Rev. **121**, 1090 (1961).

<sup>8</sup>J. Friedel, Philos. Mag. **43**, 153 (1952).

<sup>9</sup>N. F. Mott, Adv. Phys. **13**, 325 (1964).

<sup>10</sup>T. Suzuki, J. Phys. Soc. Jpn. **43**, 869 (1977).

<sup>11</sup>S. Arajs and W. E. Katzenmeyer, J. Phys. Soc. Jpn. **23**, 932 (1967).