Magnetic susceptibility of chromium-ruthenium alloys between 300 and 600 K

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Magnetic susceptibility χ of chromium-ruthenium alloys containing 0.9-, 2.1-, 3.0-, 4.8-, 6.6-, 8.3-, and 10.1-at.% ruthenium has been measured as a function of temperature T between 300 and 600 K. Each of the χ vs T curves exhibits a well-defined knee at the Néel temperature T_N. Experimental results indicate that there is no localized magnetic moment on ruthenium atoms above T_N. The temperature dependence in the antiferromagnetic region between 350 K and T_N is described by extending the Fedders-Martin theory for itinerant-electron antiferromagnets.

INTRODUCTION

Investigations[1,2] of the electrical resistivity ρ of binary chromium alloys containing ruthenium up to 14 at.% have clearly revealed very large anomalies in the neighborhood of their Néel temperatures T_N. In fact, the increases in the electrical resistivity below T_N are the largest ever observed in any binary chromium alloys except certain chromium-iron solid solutions.[3] At the present time there are no quantitative theories for such a behavior of the electrical transport properties in the neighborhood of T_N of chromium alloys. According to the above studies, T_N of chromium-ruthenium alloys increases rapidly with increasing ruthenium concentration reaching a maximum of about 555 K at the 3.5-at.% level. Addition of ruthenium above this concentration gradually decrease the values of T_N back to room temperatures.

The magnetic susceptibility χ of binary chromium alloys has not been studied extensively before. The only previous work on the chromium-ruthenium system from this viewpoint is that due to Booth,[4] and Bender and Müller.[5] Booth reports in a short letter the effects of ruthenium concentration on T_N of chromium which are in good agreement with the findings of the electrical studies mentioned above. Because chromium possesses such a unique antiferromagnetic structure, it seems that careful magnetic susceptibility studies of binary chromium alloys would be of considerable interest for further understanding of the itinerant-electron antiferromagnetism. Recently we have initiated such studies on numerous binary chromium systems. Our results on the chromium-cobalt system, where localized moments exist on cobalt atoms, has been briefly reported before.[6] In this paper, we present the magnetic-susceptibility studies on chromium-ruthenium alloys and discuss their significance.

EXPERIMENTAL CONSIDERATIONS

All the alloys used in this investigation are the same as those used in the previous electrical-resistivity studies.[1,2] The susceptibility samples having dimensions approximately $3\times3\times15$ mm were cut from the arc-melted ingots also used for the transport property work.

The susceptibilities were determined using the Faraday method. Force measurements were made with an Ainsworth type 15 electrobalance. The signal output from the balance was read on a Hewlett-Packard 3439 digital voltmeter coupled to a Hewlett-Packard 3443-A range unit. The sensitivity of this system was 10 μg.

Samples were suspended in the magnetic field ($HdH/dz \approx 4\times10^6$ Oe^2 cm^{-1}) in a quartz bucket which was connected to the balance by quartz-rod links. Temperatures between 300 and 650 K were produced by a bifilarly-wound (nickel chromalloy) furnace. The interior of the furnace could be evacuated and subsequently filled with gaseous argon. The temperatures were controlled to within ±0.01 K in the lower-temperature region and ±0.1 K for temperatures above about 500 K. Temperatures were measured using Chromel-Alumel thermocouples. The temperature control was achieved by a modular M-Line Leeds and Northrup assembly.

RESULTS AND DISCUSSION

The mass magnetic susceptibility of chromium and chromium-ruthenium alloys containing 0.9-, 2.1-, 3.0-, 4.8-, 6.6-, 8.3-, and 10.1-at.% ruthenium is shown in Fig. 1. There is a small anomaly at T_N of pure chromium which has been recently studied in considerable detail.[7] As can be seen from Fig. 1, additions of ruthenium make this anomaly more pronounced at their respective T_N. The values of T_N can be obtained from Fig. 1 as temperatures at which the χ-vs-T curves exhibit a knee. These temperatures are listed in Table I and shown in Fig. 2 in comparison with the values of T_N determined from the previous electrical-resistivity studies.[2] The agreement between the two determinations is satisfactory.

Figure 1 shows that small amounts of ruthenium rapidly increase T_N of chromium reaching a maximum value of 555 K at about 3.5 at.% level. Larg-

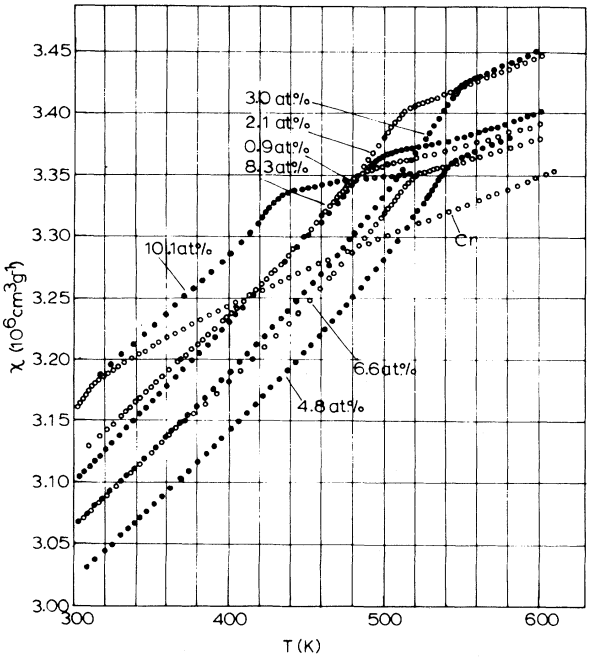

FIG. 1. Magnetic susceptibility of chromium-ruthenium alloys between 300 and 600 K. Only a representative set of data points are shown.

er ruthenium concentrations cause a gradual decrease in T_N. Speculations have been made that this behavior results from the crossover of the electron and hole Fermi surfaces[4] or from the delocalization effects of the d-electron wave functions.[8] However, it appears that, at the present time, there is no theory which could satisfactorily explain the above behavior.

The most conventional interpretation of magnetic-susceptibility data on dilute alloys is to assume that the total mass magnetic susceptibility of a particular alloy consists of two components, the susceptibility of the matrix χ_0 and the susceptibility of the solute impurity χ_{Ru}. Then

$$\chi = W\chi_{Ru} + (1 - w)\chi_0, \tag{1}$$

where w is the weight fraction of ruthenium in chromium. If it is assumed that the contribution

TABLE I. Néel temperatures of chromium-ruthenium alloys.

Ru concentration (at.%)	T_N (K)
0.9	498
2.1	512
3.0	551
4.8	544
6.6	521
8.3	483
10.1	436

χ_0 is independent of the solute concentration and equal to that of pure chromium, above T_N in all the alloys, then from Eq. (1) it is possible to calculate χ_{Ru}. This type of analysis has been recently applied by us to the chromium-cobalt system,[6] clearly indicating that a localized magnetic moment exists on cobalt atoms. Such an analysis gives χ_{Ru} independent of temperature for all ruthenium concentrations except 0.9 at.%. For this latter sample, χ_{Ru} decreases slightly with increasing temperature but does not follow a well-defined Curie-Weiss law. This strongly suggests that there is no localized magnetic moment on ruthenium atoms at least above T_N. Thus the magnetic properties of the above chromium-ruthenium alloys should be analyzed from the viewpoint of an itinerant-electron antiferromagnetism. Attempts to obtain a theory of such itinerant-electron antiferromagnets have been made by Zuckermann,[9] Fedders and Martin,[10] Maki and Sakurai,[11] and Crisan.[12]

According to the two-band model of Fedders and Martin, the magnetic susceptibility (to the first order of their calculations) above T_N should be constant. Below T_N, the magnetic susceptibility is depressed because of the gap energy which keeps the spins antiferromagnetic. If one assumes a linearly polarized spin-density wave in y direction, then the parallel and perpendicular components of the magnetic susceptibility are

$$\chi_{\parallel} = \chi_{yy} \quad \text{and} \quad \chi_{\perp} = \chi_{xx} = \chi_{zz}\,, \tag{2}$$

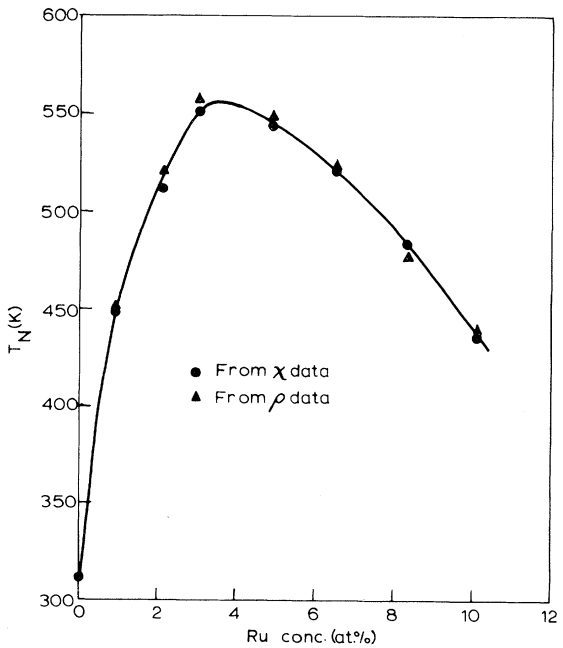

FIG. 2. Néel temperatures of chromium-ruthenium alloys.

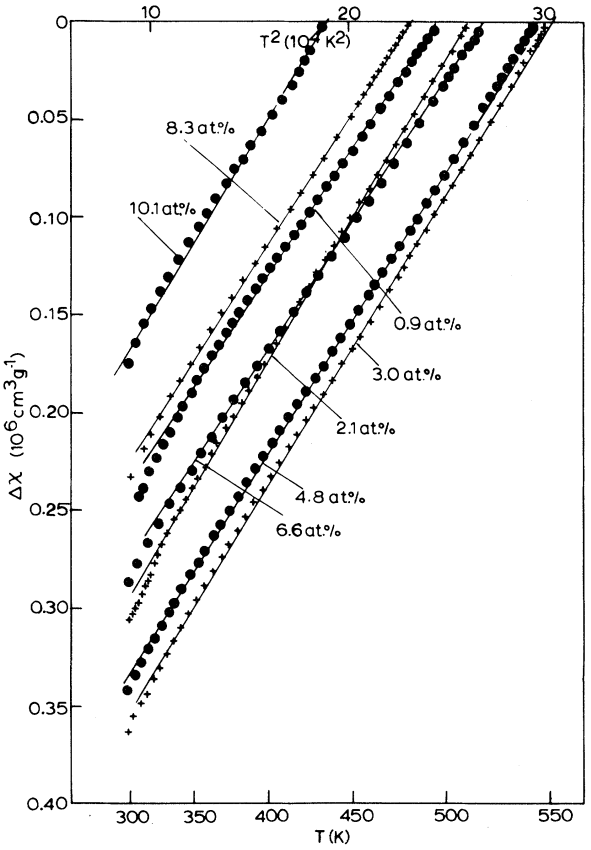

FIG. 3. $\Delta\chi$ as a function of T^2 for chromium-ruthenium alloys.

such that the total susceptibility for a polycrystalline material is

$$\chi = \tfrac{1}{3}\chi_{\parallel} + \tfrac{2}{3}\chi_{\perp} . \tag{3}$$

Fedders and Martin find that just below T_N, i.e., for $T_N - T \ll T < T_N$,

$$\chi_{zz} = \chi_{xx} = \chi_{zz}(T_N)[1 - 2(1 - T/T_N)]. \tag{4}$$

Since the anisotropy vanishes at the transition temperature, $\chi_{yy} = \chi_{zz}$ is also valid.

We extend this theory to obtain slightly different results which are in better agreement with experiment. The exact expression for χ_{yy} according to Fedders and Martin is

$$\chi_{yy} = \frac{2\mu_B^2}{(2\pi)^3}\int d^3k \frac{\partial}{\partial E}(\tanh\tfrac{1}{2}\beta E), \tag{5}$$

where μ_B is the Bohr magneton,

$$E^2 = \epsilon^2 + g^2 ,$$

and (6)

$$\epsilon = v(k - k_c),$$

$$\beta = 1/k_B T.$$

The quantity g is the gap function, v is the Fermi velocity, k_c the radius of electron (hole) Fermi sphere, k the magnitude of the wave vector, and k_B the Boltzmann constant. The corresponding expression for the component χ_{zz} derived by Fedders and Martin is

$$\chi_{zz} = \frac{2\mu_B^2}{(2\pi)^3}\left[\int d^3k \left(\frac{g^2}{E^3}\tanh\tfrac{1}{2}\beta E - \frac{g^2}{E^2}\frac{\partial}{\partial E} \times (\tanh\tfrac{1}{2}\beta E)\right) + \int d^3k \frac{\partial}{\partial E}(\tanh\tfrac{1}{2}\beta E)\right]. \tag{7}$$

By differentiating the gap equation, Eq. (7) can be reduced to the form

$$\chi_{zz} = \left(1 + \frac{g}{\beta}\frac{d\beta}{dg}\right)\chi_{yy} . \tag{8}$$

In the high-temperature regime below T_N, the second term is negligible and

$$\chi_{yy} \approx \chi_{zz} \approx \chi_{xx} \approx \chi_0[1 + \tfrac{1}{3}\pi^2(k_B T/v k_c)^2] , \tag{9}$$

correct to order $(g/k_B T)^2$. The quantity χ_0 is the Pauli magnetic susceptibility given by

$$\chi_0 = [2\mu_B^2/(2\pi)^3]\, 8\pi k_c^2/v . \tag{10}$$

One should note that the magnetic susceptibility at T_N is larger than χ_0, i.e., $\chi(T_N) > \chi_0$. To the same order, Fedders and Martin predict only a

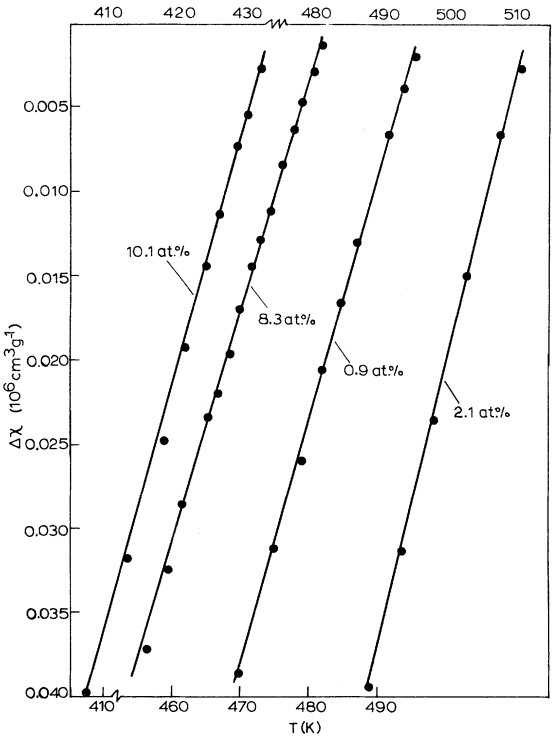

FIG. 4. $\Delta\chi$ as a function of T for chromium-ruthenium alloys containing 0.9-, 2.1-, and 10.1-at.% ruthenium.

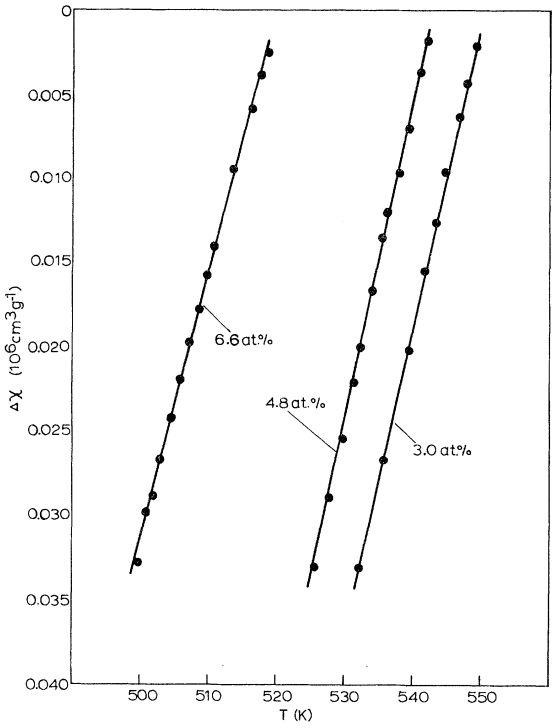

FIG. 5. $\Delta\chi$ as a function of T for chromium-ruthenium alloys containing 3.0-, 4.8-, and 6.6-at.% ruthenium.

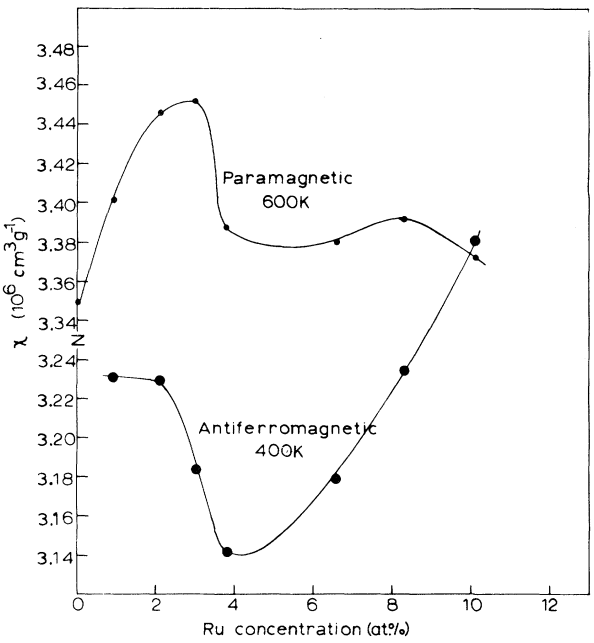

FIG. 6. χ of chromium-ruthenium alloys as a function of ruthenium concentration at 400 and 600 K.

constant term. The second term which is ($\sim k_B T/d$ – band width)^2 represents a correction of only about 1.0%. Nevertheless, this term is vital to a proper interpretation of the experimental results.

Equation (9) implies that the quantity $\Delta\chi = \chi(T_N) - \chi$ (where χ is the magnetic susceptibility below T_N), representing the decrease in χ below T_N, should be proportional to T^2. Since g is only about 0.02 eV even at absolute zero, this conclusion should hold down to about room temperatures. Figure 3 shows $\Delta\chi$ as a function of T^2. It can be seen that these plots are approximately straight lines except for small curvatures below about 350 K. Figures 4 and 5 show $\Delta\chi$ as a function of T just below T_N. These plots indicate that about 20 K below T_N, $\Delta\chi$ is proportional to T, as would be expected from a Taylor expansion near T_N using the above extension of the Fedder-Martin theory. Thus, it appears that this theory accounts reasonably well for the observed temperature dependence of χ of chromium-ruthenium alloys below T_N.

In general, the total value of χ at some particular temperature above T_N of chromium-ruthenium alloys should be made up of the diamagnetic contribution of the closed shells constituting the core of each atom, the diamagnetism due to the conduction electrons in s and d bands, the Van Vleck susceptibility due to the orbital motion of the d electrons, and the Pauli paramagnetic susceptibility. The last contribution is related to the density of states at the Fermi energy. Figure 5 shows the total χ of chromium-ruthenium alloys in the paramagnetic region at 600 K as a function of the ruthenium concentration. Whether the features of this curve are related to the density of states values is difficult to say because of the other magnetic contributions mentioned above. It should be mentioned that various oscillations in the χ-vs-concentration curve have been seen in the chromium-vanadium system,[13] and have been, at least partially, related to the electronic structure of the system. Figure 6 also

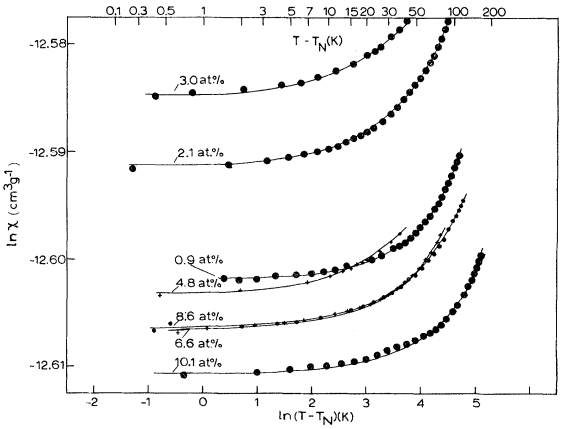

FIG. 7. $\ln\chi$ as a function of $\ln(T - T_N)$ for chromium-ruthenium alloys above T_N.

presents χ of chromium-ruthenium alloys in the antiferromagnetic state at 400 K. The behavior of this curve is completely different from that in the paramagnetic case. The reasons for the observed minimum at about 5-at.% ruthenium are not understood at this time.

In principle, it would be interesting to determine the critical exponents, characterizing the antiferromagnetic-paramagnetic transitions of the chromium-ruthenium system. Unfortunately, this requires very accurate determination of T_N. Our χ studies indicate that this is difficult to do for the chromium-ruthenium alloys. It is well known that the paramagnetic susceptibility of ferromagnets above the ferromagnetic Curie temperature T_C can be represented by a power law of $T - T_C$. For example, iron obeys such a law[14] with the exponent close to $-\frac{4}{3}$. Phenomenologically, the paramagnetic behavior of χ of the chromium-ruthenium alloys can be analyzed in this fashion. Figure 7 shows $\ln\chi$ vs $\ln(T - T_N)$ for the chromium-ruthenium alloys above T_N. The values of T_N used in this plot are those given in Table I. From Fig. 7 it can be seen that for temperatures between about 0.3 and 5 K, above T_N, χ for all alloys is proportional to $(T - T_N)^\gamma$, where $\gamma \approx 0.7 \pm 0.2$.

ACKNOWLEDGMENT

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