ANOMALIES IN THE ELECTRICAL RESISTANCE OF Al:Mn AND Al:Cr ALLOYS

A. D. Caplin
Department of Physics, Imperial College, London SW7, England

and

C. Rizzuto
Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche,
Istituto di Fisica dell'Università, Genova, Italy

(Received 29 April 1968)

Measurements of the low-temperature impurity resistance of dilute Al:Mn and Al:Cr alloys indicate a form $\rho(T)=\rho_0[1-(T/\theta)^2]$ where $\theta\approx 530$°K for Mn and 1200°K for Cr, and this behavior can be correlated with the high-temperature enhanced Pauli susceptibility of these alloys using the localized spin-fluctuation concept.

The occurrence of magnetic or nonmagnetic behavior of the $3d$ transitional impurities dissolved in mono-, di-, and trivalent simple metals (e.g., Cu, Zn, Al) has been qualitatively explained by Friedel[1] and Anderson,[2] and there is an understanding of why systems such as Zn:Fe, Al:Mn, and Al:Cr display none of the striking "magnetic" symptoms that are found in, for example, Cu:Mn. However, recent measurements[3] have shown the presence of a weak low-temperature resistance minimum (one of the characteristic features of a magnetic impurity) in Zn:Fe, and have therefore prompted us to utilize the inherent accuracy of resistance measurements to examine Al:Mn and Al:Cr for similar small effects.

The alloys used were drawn into wires 0.3 to 0.6 mm in diameter and 20 to 100 cm long and annealed at 630°C and quenched into water. The quantity measured was the ratio of the voltages developed across the transition alloy sample and a standard sample of similar resistance of an Al:0.43 at.% Cu alloy (which should show no anomaly), the two samples being connected in series and both immersed in the liquid-helium bath; by switching back and forth from one sample to the other at regular intervals the effect of drifting currents and thermal emf's could be reduced, and under favorable conditions measurements of the voltage ratio show a scatter of less than one part per million. We have also measured the 1.5 to 4.2°K temperature dependence of the Al:Cu sample resistance by comparing it with a second normal alloy (Al:0.22 at.% Zn) and assuming that Matthiessen's rule holds for these two alloys; we find that we can fit the resistivity with $\rho=\rho_0+AT^3$ where $A=(1.5\pm0.1)10^{-13}$ Ω cm °K^{-3}, which is almost identical to the low-temperature lattice resistivity found for pure Al.[4] From the voltage ratio of the transitional and standard samples and the temperature dependence of the standard sample we obtain the resistance of the transitional sample as a function of temperature (Fig. 1); above 3°K the dominant uncertainty is that in the lattice resistance of the standard sample. Finally we subtract the lattice resistivity of the transitional sample itself, which we assume equal to that of the normal alloys, in order to obtain the transitional impurity resistance (Fig. 1).

The relative change in impurity resistance with temperature for the Al:Mn alloys shows a T^2 dependence that is substantially independent of concentration (Fig. 2), thus justifying our assumptions about subtraction of the lattice resistivity. The Al:Cr samples show a weaker temperature dependence which is perhaps again of a T^2 form. The behavior of the observed resistivity can be

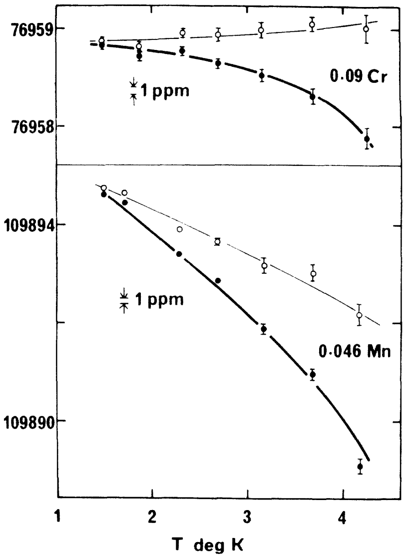

FIG. 1. Electrical resistance (arbitrary units) versus temperature of the most dilute Al alloys. Open circles, measured resistance; filled circles, impurity resistance, equal to the measured resistance minus lattice resistance.

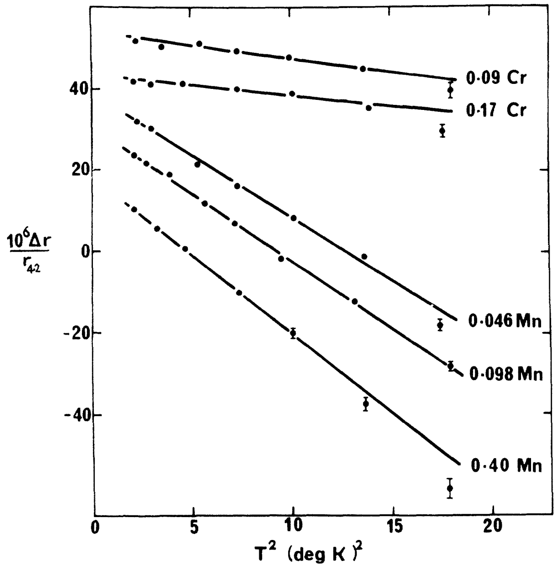

FIG. 2. Relative change in impurity resistance (in parts per million) of Al:Mn and Al:Cr alloys versus square of temperature. The vertical position of each curve is arbitrary.

summarized as

$$\rho(T)=\rho_0[1-(T/\theta)^2], \qquad (1)$$

where ρ_0 and θ are shown in Table I.

One possible explanation of this behavior involves the Nagaoka[5] condensation, and a resistivity of similar form to Eq. (1) has indeed been suggested[6] with $\theta\approx T_K$, where kT_K is of the order of the binding energy of the condensed state. However, if a condensation is responsible, large changes in the impurity resistance and magnetic susceptibility should occur at temperatures of order T_K, but experimentally both the resistivity[7] and susceptibility[8-10] of Al:Mn and Al:Cr are essentially constant near room temperature, so that at least for Al:Mn the anomalous term in the resistivity has disappeared at temperatures of order θ, which argues against the condensation hypothesis.

As an alternative explanation we note that a T^2 dependence is characteristic of thermal smearing, and application of the standard Sommerfeld expansion to the scattering cross-section of a resonant (half-filled, as is appropriate[7] for Mn and Cr in Al) Lorentzian virtual bound state (v.b.s.) of width Δ yields

$$\rho(T)=\rho_0[1-(\pi^2/3)(kT/\Delta)^2].$$

The Pauli susceptibility of such a system with fivefold orbital degeneracy is

$$\chi_{\mathrm{P}}^{\,0}=(10N\mu_{\mathrm{B}}^{\,2}/\pi)1/\Delta.$$

However, if the impurity is near to being magnetic, the susceptibility is enhanced:

$$\chi_{\mathrm{P}}=\eta\chi_{\mathrm{P}}^{\,0}=(10N\mu_{\mathrm{B}}^{\,2}/\pi)\eta/\Delta \qquad (2)$$

with $\eta=(1-u/\pi\Delta)^{-1}$ in the case of an orbitally nondegenerate impurity containing one electron (where U is an intraimpurity Coulomb energy), and we suggest that just as Δ/η is the effective width for the susceptibility it is also appropriate for the thermal smearing of the scattering cross-section, so that

$$\rho(T)=\rho_0[1-(\pi^2/3)(\eta kT/\Delta)^2]; \qquad (3)$$

or, in terms of the parameter θ,

$$\Delta/\eta=\pi k\theta/\sqrt{3}. \qquad (4)$$

Thus from the experimental values of χ_{P} and θ we can obtain two independent estimates of the quantity Δ/η shown in Table I; the only approximation we have made is one to which Eq. (3) is insensitive: that the v.b.s. is Lorentzian and half-filled. Since there are no adjustable parameters the good numerical agreement provides strong evidence for the connection between susceptibility and resistivity.

Table I. Properties of Al:Mn and Al:Cr alloys.

Alloy	ρ_0 ($\mu\Omega$ cm/at.%)	θ, Eq. (1) (°K)	χ_{P} (10^{-6} emu/mole)	Δ/η (10^{-2} eV) From resistivity, Eq. (4)	From susceptibility, Eq. (2)
Al:Mn	8.0[a]	530 ± 30	1200 ± 100[b]	8.3 ± 0.5	8.6 ± 0.7
			1115 ± 30[c]		9.0 ± 0.2
			1500 ± 200[d]		6.9 ± 1.0
Al:Cr	8.4[a]	1200 ± 400	300 ± 50[b]	20 ± 7	30 ± 5
			700 ± 50[c]		15 ± 1
			700 ± 150[d]		15 ± 3

[a] From Ref. 7. [b] From Ref. 8 at 300°K. [c] From Ref. 9 at 1360°K (liquid Al). [d] From Ref. 10 at 300°K.

We propose a simple physical justification for our conjecture: Consider a Friedel-Anderson nonmagnetic v.b.s. ($U<\pi\Delta$). In its ground state it contains an equal number of localized spin-up and spin-down electrons, but excitations with an unequal number become of lower and lower energy as U approaches $\pi\Delta$ (the Friedel-Anderson condition for the impurity to become magnetic), so that the effect of any perturbation of the spins becomes enhanced, and we argue that this enhancement is the same whether the perturbation is dynamic or static. At a finite temperature and with $U=0$ the spin-up and spin-down populations would fluctuate by an amount corresponding to moving the v.b.s. $\sim kT$ in energy, and because there is no correlation the difference in populations would fluctuate by a similar amount; however, if U is finite the spins up and down are correlated in a "see-saw" fashion so that the amplitude of the fluctuations is of order ηkT, where η is the same factor as that which enhances the static population difference induced by a steady magnetic field. The scattering cross section for conduction electrons of each spin is related via the phase shift to the v.b.s. occupation of that spin,[1] so it is thermally averaged over an energy range $\sim\eta kT$, and we are immediately led to Eq. (3). Furthermore, since Δ measures the rate at which conduction electrons hop on and off the v.b.s., we would expect the inverse correlation time $\tau_{\text{l.s.f.}}^{-1}$ of these localized spin fluctuations[11] (l.s.f.) to be measured by Δ/η. The time scale of the l.s.f. is clearly important, for we have so far implied that the resistivity is determined by only the time-average cross section and the susceptibility by the time-average polarization, and this will be valid only if the l.s.f. are fast compared with other relevant times. On the other hand, if the l.s.f. are slow enough (i.e., if the impurity is very close to the Friedel-Anderson critical condition), its temporary magnetic moment may have sufficient time to equilibrate in an applied magnetic field or to flip the spin of a conduction electron, and so will contribute a Curie susceptibility and a logarithmic resistivity: An impurity in the slow l.s.f. regime therefore appears to be (weakly) magnetic (Zn:Fe may be an example of this situation[3]). Finally, we suggest that l.s.f. may also account for the observed anomalies in thermoelectric power[12] and depression of the superconducting transition temperature[13] of these alloys.

The concept of localized spin fluctuations, which has been given formal justification by Rivier, Zuckermann, and Šunjić,[11] overcomes the sharp and unphysical boundary between magnetic and nonmagnetic impurities in the Friedel-Anderson theory by replacing it with a smooth transition between slow and fast l.s.f. regimes. The Nagaoka condensation,[5] which is based on a very different approach, also provides a smooth transition and Rivier[14] has recently shown that fast l.s.f. are equivalent to condensation with high T_K, but it seems to us that the physical interpretation of the l.s.f. concept is considerably more transparent than that of the condensation.

We have benefited from stimulating conversations with Professor P. W. Anderson and Professor B. R. Coles (who also helped us with the measurements), and with Dr. N. Rivier and Dr. M. J. Zuckermann. Mr. A. A. Parodi assisted us with the sample preparation, and some of the alloys were kindly provided by Istituto Sperimentale Metalli Leggeri, Novara, Italy.

---

[1] J. Friedel, Nuovo Cimento Suppl. 7, 287 (1958).

[2] P. W. Anderson, Phys. Rev. 124, 41 (1961).

[3] A. D. Caplin, Phys. Letters 26A, 46 (1967).

[4] E. W. Fenton, J. S. Rogers, and S. B. Woods, Can. J. Phys. 41, 2026 (1963); R. Stevenson, Can. J. Phys. 45, 4115 (1967); W. B. Willott, Phil. Mag. 16, 691 (1967).

[5] Y. Nagaoka, Phys. Rev. 138, A1112 (1965).

[6] Y. Nagaoka, J. Phys. Chem. Solids, 27, 1139 (1966).

[7] G. Boato, M. Bugo, and C. Rizzuto, Nuovo Cimento 45B, 226 (1966).

[8] M. Taylor, J. P. Burger, and J. Wucher, J. Phys. Radium 20, 829 (1959).

[9] C. P. Flynn, D. A. Rigney, J. A. Gardner, Phil. Mag. 15, 1255 (1967).

[10] R. Aoki and T. Ohtsuka, to be published.

[11] N. Rivier, M. Zuckermann, and M. Šunjić, to be published.

[12] G. Boato and J. Vig, Solid State Commun. 5, 549 (1967).

[13] G. Boato, G. Gallinaro, and C. Rizzuto, Phys. Rev. 148, 353 (1966).

[14] N. Rivier, private communication.