March 1969

Local Moment Formation and Resistivity Minima in CoAl Alloys

G.R. Caskey
Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts

David J. Sellmyer
University of Nebraska-Lincoln, dsellmyer@unl.edu

JOURNAL OF APPLIED PHYSICS VOLUME 40, NUMBER 3 1 MARCH 1969

Local Moment Formation and Resistivity Minima in CoAl Alloys*

G. R. CASKEY AND D. J. SELLMYER

Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Measurements of electrical resistivity, thermoelectric power, and magnetoresistance have been made from 1.4° to 300°K in alloys of 48%–57% cobalt in aluminum. At the equiatomic composition, CoAl has the CsCl structure. Resistance minima were observed in the vicinity of 30°K for cobalt concentrations between 50.4% and 51.5%. Below the resistance minima there is a temperature region where the dependence is approximately logarithmic before it saturates at about 1.4°K. The depth of the minima $[\rho(1.4°K)-\rho(T_{min})]$ and the thermopower at 4.2°K both show rather sharp peaks as a function of concentration in the vicinity of 50.5% cobalt. The magnetoresistance of the samples showing minima is negative for $T<T_{min}$ and its magnitude increases with field up to 150 kG. These results and earlier susceptibility measurements for this system are discussed in terms of several current theories of the electronic effects of magnetic impurities in metals.

There have been many observations of anomalies in the low-temperature electronic properties of metals with small concentrations of magnetic impurities. In the present work, similar effects are reported in concentrated alloys of cobalt in aluminum. The cobalt concentration c, in atomic percent, ranged from 48–57. At the equiatomic composition the alloy has the ordered CsCl structure which is simple cubic with the aluminum and cobalt atoms at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(0, 0, 0)$ positions, respectively. It is known that for $57 \gtrsim c > 50$, cobalt atoms replace aluminum atoms substitutionally whereas for $47 \lesssim c < 50$, the cobalt deficiency is achieved through vacancies on cobalt sites.[1] The interesting magnetic effects occur for c slightly larger than 50 so that, for this concentration range, the alloy *might* be regarded as a dilute solid solution of cobalt atoms in the ordered metallic compound CoAl.

EXPERIMENTAL RESULTS

Figure 1 shows the temperature dependence of the resistance ratio, $r(T) \equiv R(T)/R(4.2°K)$, for $49 \lesssim c \lesssim 51.9$. Specimens in the range $50.4 \leq c \leq 51.5$ exhibit a resistance minimum at a temperature T_{min} in the vicinity of 30°K. Both T_{min} and the depth of the minimum are dependent upon composition. Except for Co(50.4), $r(T)$ has reached a constant value at 1.4°K. The temperature dependence of $r(T)$ for the samples showing a minimum is approximately logarithmic in the middle portion of the interval between 1.4°K and T_{min}.

The transverse magnetoresistance $(\Delta\rho/\rho)$, measured between 1.6° and 77°K, is negative at all fields up to 150 kG for alloys with $c > 50$. For Co(49.0) the magnetoresistance is positive except at the lowest fields and for all samples, the magnitude does not saturate at 150 kG.

Figure 2 shows the composition dependence of the thermoelectric power at 4.2° and 296°K. The rather sharp structure exhibited, in particular, at 4.2°K occurs for the same compositions that show resistivity minima. The sample that shows the strongest resistance minimum, Co(50.4), also shows a positive peak in the thermopower at 7°K which is roughly at the midpoint of the resistivity rise for this specimen.

The susceptibility of this alloy system was measured at 5 kG between 77° and 300°K by West.[2] In this temperature range, χ is essentially independent of temperature for $c = 49.4$. For $c = 50.8$ and 51.2, χ follows an antiferromagnetic Curie–Weiss law, and for $52.8 \leq c \leq 54.5$ a ferromagnetic Curie–Weiss law. The magnetization of specimen Co(50.4) was measured at 4.2°K in fields up to 50 kG[3] and was proportional to $(\Delta\rho/\rho)^{1/2}$. The susceptibility was a decreasing function of field and the limiting value of $d\sigma/dH$ was 9.4×10^{-6} emu/g at 50 kG.

DISCUSSION

In light of the temperature and concentration dependence of χ, and the sign of the magnetoresistance, it may be hypothesized that for $c \leq 50$ there are no localized moments and that for c slightly larger than 50, magnetic moments exist on the excess cobalt atoms. This hypothesis seems reasonable since, for $c < 50$ *none* of the cobalt atoms has nearest neighbors which are not aluminum atoms. However, for $c > 50$ the excess cobalt atoms exist at the center of a cube with eight nearest-neighbor *cobalt* atoms at the corners, a structure that would seem to be conducive to the formation of a local moment on the excess cobalt atoms.

In view of the approximate logarithmic temperature dependence of the resistivity, it is natural to ask whether the data can be explained in terms of the Kondo effect[4]

* This research was supported by the Advanced Research Projects Agency and was performed in part at the Francis Bitter National Magnet Laboratory which is supported by the U.S.A.F.O.S.R.

[1] N. Ridley, J. Inst. Metals **94**, 255 (1966).

[2] G. W. West, Phil. Mag. **15**, 855 (1967).

[3] These measurements were made by S. Foner and I. De Grave.

[4] J. Kondo, Progr. Theoret. Phys. **32**, 37 (1964).

in which the excess cobalt atoms would have to be considered as the "impurity" atoms in the "pure" metallic compound. If we take this point of view and let the atomic percent of the impurity atoms be denoted by $x \equiv c-50$ for $c \geq 50$, then the Kondo theory would imply that $\rho_{\text{spin}} \propto x$. Taking $\rho_{\text{spin}} = \rho(T) - \rho(T_{\text{min}})$ gives $\rho_{\text{spin}}/x \simeq$ constant for $x=0.4$ and 0.6 but not for larger x. For larger x, interactions between the impurity atoms would presumably become important and, in fact, the susceptibility data suggest that the alloy becomes ferromagnetic at low temperatures between 52% and 53% cobalt.

There are, however, other theories which may be relevant to this system. For example, the theory of localized spin fluctuations of Rivier *et al.*,[5] predicts a weak resistance minimum with a low-temperature logarithmic dependence, antiferromagnetic Curie–Weiss behavior in the susceptibility, and a tendency towards a giant thermopower as the lifetime of the spin fluctuations becomes large. Clearly, our data on the depth of the resistance minimum $[\rho(1.4°\text{K}) - \rho(T_{\text{min}})]$ as well as the thermopower at 4.2°K show sharp peaks at a concentration of about 50.5% cobalt. If localized spin fluctuations are important in this system, then this would suggest that $c \simeq 50.5$ is the critical concentration at which the impurity states approach the magnetic limit.

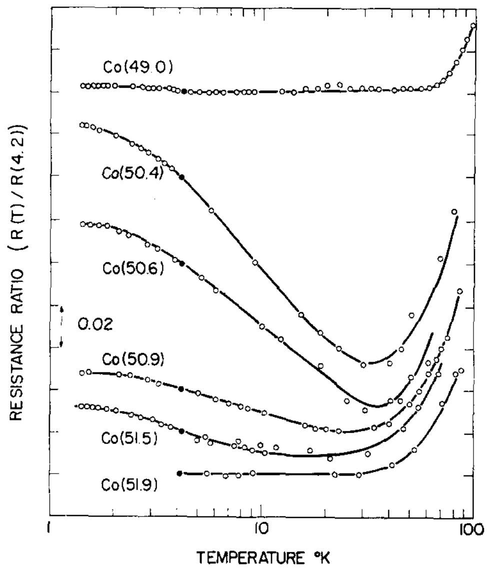

FIG. 1. Temperature dependence of the resistance ratio $R(T)/R(4.2)$. The vertical placement of the curves is arbitrary but the solid points show where the ratio is defined to be unity.

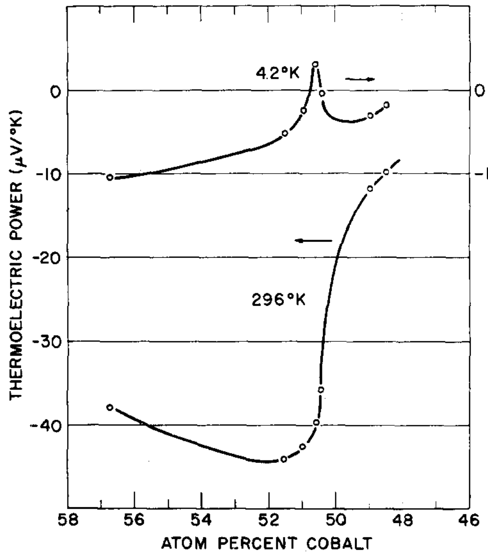

FIG. 2. Thermoelectric power vs composition.

A further possible explanation, perhaps, is that localized moments exist not only on the excess cobalt atoms, but also on their eight nearest-neighbor cobalt atoms. From the susceptibility data in the range $50.8 < c < 53$, one can derive an effective magnetic moment of 8.9 Bohr magnetons per excess cobalt atom. If, in fact, the neighbors of the impurity cobalt atoms are magnetic, then it would be necessary to consider the interaction of the conduction electrons with interacting impurity pairs or even multiple spin complexes. Dekker, Brailsford and Overhauser, and others have considered the interaction of the conduction electrons with coupled impurity spins and this theory also can predict a resistance minimum and negative magnetoresistance under certain circumstances.[6] Obviously, a detailed interpretation of these results will have to rely on further low-temperature susceptibility data and also microscopic magnetic measurements.

We wish to thank Dr. D. J. Kim for several helpful discussions.

[5] N. Rivier, M. J. Zuckerman, and M. Sunjic (unpublished); see also: D. J. Kim, Phys. Rev. **146**, 455 (1966).

[6] For a review of these theories, see: T. Van Peski-Tinbergen and A. J. Dekker, Physica **29**, 917 (1963).