Order-disorder and α-γ transitions in FeCo†

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Electrical resistivity (ρ) measurements in an FeCo alloy (with 47.63-wt.% of Co) in the temperature range of 500–1350 °K are reported. Special attention is given to the temperature regions of 900–1100 °K and 1160–1300 °K. A change in the slope of the ρ vs T curve, associated with the order-disorder transition, yields a λ-type anomaly in $\partial\rho/\partial T$ with maximum at $T \simeq 1006$ °K. Comparison with the specific heat $C(T)$ data of Orehotsky and Schröder shows that $\partial\rho/\partial T$ is proportional to $C(T)$ in the critical region similar to the observations in β brass. Near 1230 °K, a discontinuous change in resistivity of about 20% with hysteresis of about 12 °K, is observed. This first order transition is associated with the α-γ transition.

I. INTRODUCTION

In this paper a detailed study of the order-disorder (OD) and α-γ (bcc-fcc) transition in nearly equiatomic FeCo alloy using electrical-resistivity measurements is reported. The OD transitions in solids have received considerable attention since they are expected to behave the same way mathematically near the OD transition temperature T_c as the Ising model.[1,2] In recent years many studies of the critical behavior of the OD transition in β-brass (CuZn) have been made. In a recent paper Salamon and Lederman[3] have shown that the specific-heat anomaly near T_c in β-brass does indeed follow the predictions of the three-dimensional Ising model. Also it has been observed that $\partial\rho/\partial T$ is proportional to $C(T)$ near T_c in β-brass,[4] where ρ is the electrical resistivity and $C(T)$ is the specific heat associated with the order-disorder transition. Parks has reviewed the studies on the transport properties near T_c.[5]

An OD transformation in the nearly equiatomic FeCo system has been known for quite sometime.[1,2,6] Recently Orehotsky and Schröder have studied the associated anomaly in the specific heat near T_c.[7] An anomaly in the electrical resistivity near T_c in FeCo, however, has not been observed so far.[1] First observation of such an anomaly in FeCo is reported in this paper. Computed values of $\partial\rho/\partial T$ are compared with the specific-heat measurements of Orehotsky and Schröder.[7]

A structural phase change from bcc (α phase) to fcc (γ phase) with increasing temperature is also known to occur in Fe and in FeCo alloys containing up to about 80-wt.% Co. In the present work on an FeCo alloy with 47.63 wt.% of Co (46.29 at.% of Co), about a 20% jump in the electrical resistivity is observed at the $\alpha \to \gamma$ transition. This and the observation of hysteresis suggest the transition to be of first order. It is argued that the nature of the $\alpha \to \gamma$ transition in FeCo is quite different from that in Fe. Above results are presented and discussed in this paper.

II. EXPERIMENTAL DETAILS AND PROCEDURE

The alloy of Fe and Co was prepared by arc melting equal amounts of Fe and Co rods of 99.99% purity. Chemical analysis of the resulting alloy showed it to contain 47.63 wt.% of Co. The sample was annealed in vacuum at 800 °C for four days and then cooled at the rate of about 1 °C/min down to 500 °C. The furnace was then shut off and the sample allowed to cool at the natural cooling rate of about 5 °C/min. The data were taken by bringing the sample to thermal equilibrium at each temperature, with a resolution of $\frac{1}{2}$ °C in regions of special interest. All the measurements were taken with increasing temperatures, except the data near the $\alpha \to \gamma$ transition. Here the data with decreasing temperatures were also taken in an effort to observe any hysteresis. The measurements were made using the standard four-probe technique. The leads were spot-welded and the sample measured $1.102 \times 0.430 \times 0.112$ cm^3. The temperatures were monitored with a chromel-alumel thermocouple and a K-4 potentiometer. The resistivity measurements at a given temperature were found to be reproducible to within 1 part in 10^4 at several temperatures.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The measured electrical resistivity of the FeCo sample in the temperature range from about 500 to 1350 °K is shown in Fig. 1. For reasons discussed below, special attention was given to the temperature regions from about 760 to 830 °K, 900

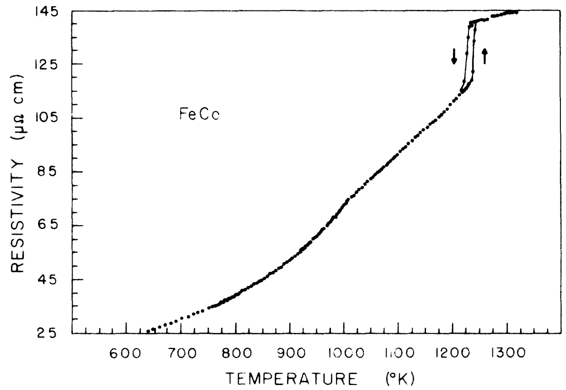

FIG. 1. Measured resistivity ρ of FeCo (46.29 at.% of Co) is plotted against temperature. For sake of clarity, all the data points are not shown.

to 1100 °K, and 1160 to 1300 °K. In these regions the data were taken at temperature steps of as close as $\frac{1}{2}$ °C. A change in the slope of the ρ vs T curve near 1006 °K is associated with the OD transition and the anomaly in ρ near 1230 °K is due to the α-γ transition. These results are discussed in detail below.

A. Order-disorder transition

The resistivity of the FeCo sample in the temperature range 900–1100 °K is shown in Fig. 2. We associate the change in the slope of the ρ-T plot near $T_c = 1006$ °K with the OD transition in FeCo since this is the correct region for the order-disorder phenomenon in this system.[6,7] We believe that this is the first such observation in this system using the temperature-dependent electrical-resistivity measurements. The observed linear variation of ρ with temperature above about 1010 °K is most likely due to the phonon contribution since for $T > \Theta_D$ (Debye temperature) the predicted phonon contribution to $\rho \propto T/nM\Theta_D^2$, where n is the density of the charge carriers and M is the ionic mass.[8] The dotted line in Fig. 2 is extrapolated from this linear dependence. It is clear from Fig. 2 that below T_c, ρ at a given temperature is lower than the extrapolated value, in agreement with the observation in β-brass for the low-temperature ($T < T_c$) ordered phase. This can be understood qualitatively if the process of ordering results in reduced resistivity due to reduction in the spin-disordering contribution to ρ.

In the analysis of the electrical-resistivity data

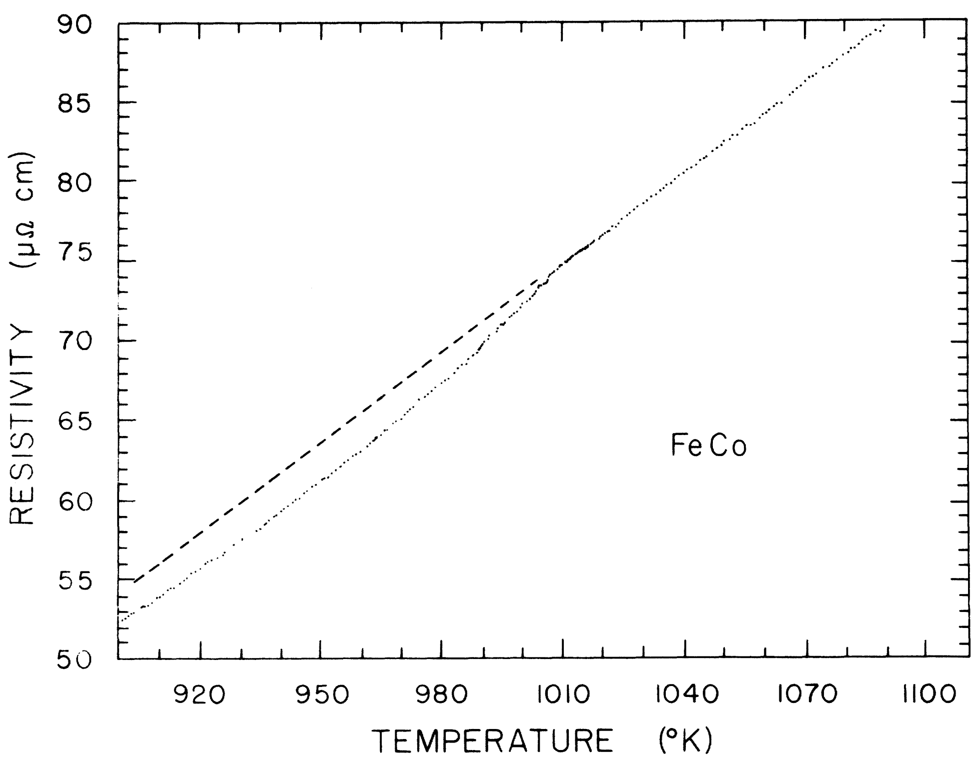

FIG. 2. Resistivity vs temperature near the order-disorder transition T_c. The dotted line is an extrapolation of the linear variation of ρ with T above T_c.

in β-brass, Simons and Salamon[3] showed that if (i) no energy gaps appear in the Fermi surface upon ordering and (ii) the Fermi surface nearly fills the zone, then the correlations between nearest neighbors dominate in spin-disorder scattering of conduction electrons. Consequently, near T_c the energy $U(T)$ associated with the OD transition and the critical electrical resistivity $\rho_c(T)$ are expected to have the same temperature dependence or equivalently the specific heat $C(T) \propto \partial\rho_c/\partial T$. In Fig. 3 we have plotted the computed values of $\partial\rho/\partial T$ using the data shown in Fig. 2 against temperature. $\partial\rho/\partial T$ was computed using a least-squares fit to second-order polynomial.[9] The shape of the anomaly in $\partial\rho/\partial T$ in Fig. 3 is very similar to that reported in the specific heat C_p by Orehotsky and Schröder.[7] The slight "bumps" in $\partial\rho/\partial T$, both above and below T_c, are most likely due to scatter in the data, and we are inclined not to attach much importance to these.

For a quantitative comparison of the prediction mentioned above, viz., $C(T) \propto \partial\rho_c/\partial T$ near T_c, we have plotted the two quantities against each other in Fig. 4. The specific-heat data is taken from the paper by Orehotsky and Schröder[7] with the phonon background subtracted out. (Note that for $T > 1.015T_c$, the actual data of C_p has considerable scatter and the values shown in Fig. 4 are the best average values taken from the graph in Ref. 7.) If $C(T) \propto \partial\rho_c/\partial T$, as observed in β-brass, then plots for $T > T_c$ and $T < T_c$ in Fig. 4 should be straight lines with slopes giving the constants of proportionality and the intercepts the constants of phonon contribution to the electrical resistivity.

We believe that based on the comparison in Fig. 4, a strong case can be made for the proportionality to be valid in FeCo near T_c, although there is scatter in the data, particularly in the C_p values. The straight lines in Fig. 4 are the least-squares fit through the points. The two slopes as well as the intercepts above and below T_c are different as in the case of β-brass. These might be related to slight changes in the lattice constants observed near T_c in both materials.

B. α-γ transition

Details of the resistivity data near the α-γ transition temperature $T_{\alpha\gamma}$ are shown in Fig. 5. Observation of the large hysteresis (~12 °K) effect and an abrupt change in ρ clearly suggest this transition to be of first order. An increase in ρ at $T_{\alpha\gamma}$ upon increasing temperatures has been indicated in the earlier reported measurements[2] although no attempt was apparently made to observe the hysteresis. If we specify $T_{\alpha\gamma}$ to be at the center of the hysteresis loop, then we find $T_{\alpha\gamma} \simeq 1235$ °K, in reasonable agreement with the earlier reports.[6] It is also noted that away from the hysteresis loop $\rho \propto T$ as expected for $T > \Theta_D$.

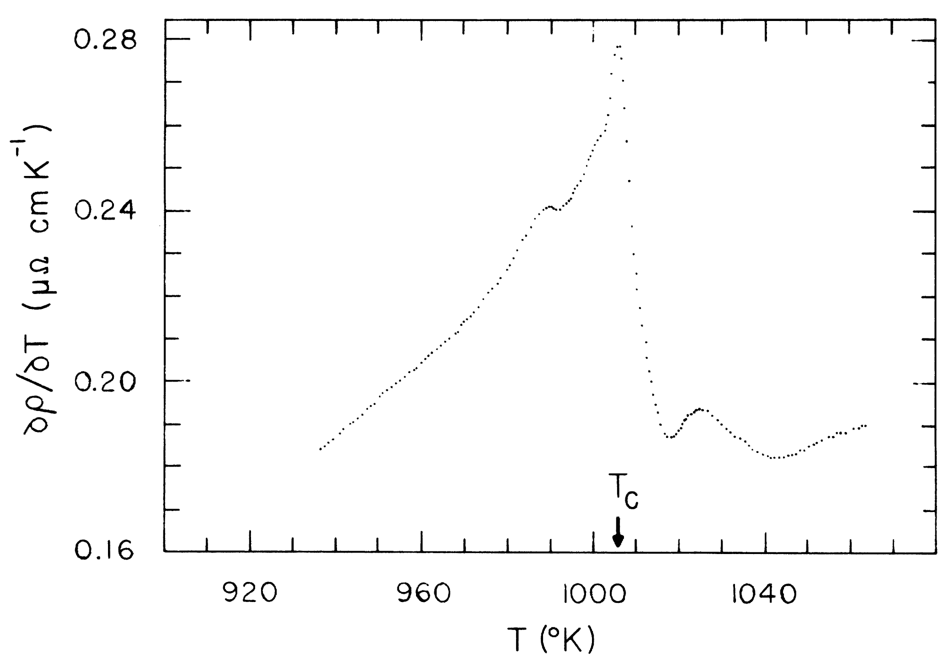

FIG. 3. Computed $\partial\rho/\partial T$ vs temperature for the FeCo alloy.

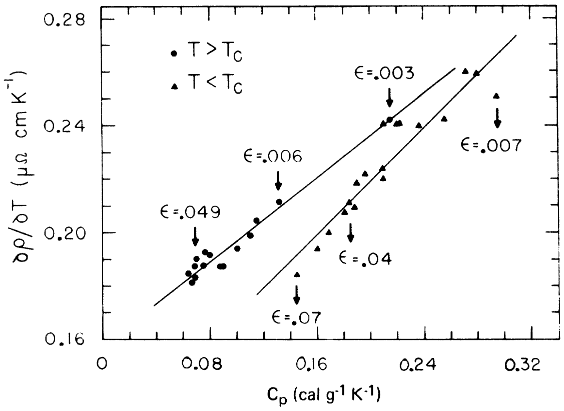

FIG. 4. $\partial\rho/\partial T$ vs specific heat at constant pressure C_p (data of Ref. 7) for different reduced temperatures $\epsilon = |(T - T_c)/T_c|$. The solid lines are least-squares fits to the data for $T > T_c$ and $T < T_c$.

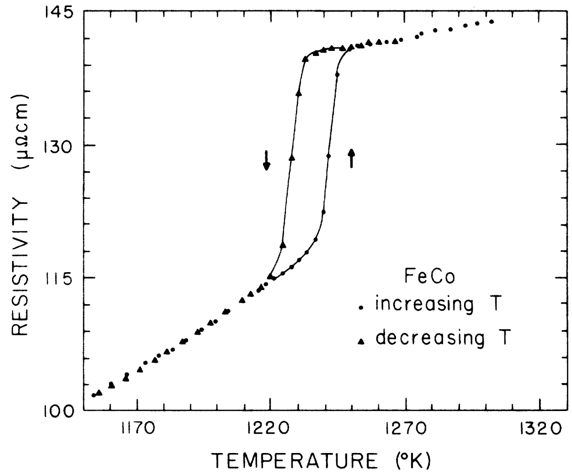

FIG. 5. Details of the resistivity near the α-γ transition. Data points were taken at time intervals of at least 5 min.

A similar α-γ structural transition also occurs in pure Fe near 1180 °K.[10] Arajs and Colvin[11] studied the behavior of the electrical resistivity of Fe through $T_{\alpha\gamma}$. They observed a hysteresis of about 2 °K and a *drop* in ρ of about 2% with increasing temperatures. For FeCo an *increase* in ρ of about 20% at $T_{\alpha\gamma}$ with increasing temperatures is observed (Fig. 5). Thus the nature of the α-γ transition in FeCo is quite different from that observed in Fe.

Let us first consider the α-γ transition in Fe. Mössbauer studies have shown[12] that about 2% jump in Θ_D(~350 °K) occurs at the $\alpha \to \gamma$ transition. Since $\rho \propto T/nM\Theta_D^2$ for $T > \Theta_D$, an increase in Θ_D would result in a decrease in ρ as observed by Θ_D Arajs and Colvin.[11] An increase in Θ_D is consistent with the observed increase in the Young's modulus at $T_{\alpha\gamma}$.[13] For a quantitative comparison a change in the density of the charge carriers n at $T_{\alpha\gamma}$ must also be taken into account, since it is known that the mean volume per atom decreases by about 2% at the α-γ transition.[10] However, changes in n are somewhat difficult to estimate for there are likely to be changes in the band structure at $T_{\alpha\gamma}$.

In the case of FeCo alloy we do not have the advantage of the knowledge of Θ_D, elastic properties, or thermal expansion near $T_{\alpha\gamma}$. However, it is possible to make some qualitative remarks regarding the difference in the behavior of the resistivity in Fe and FeCo near $T_{\alpha\gamma}$. The phonon spectrum of Fe should contain only acoustical modes, whereas in FeCo three optical modes should exist because of the two dissimilar atoms in the primitive cell. If one of these optical modes goes soft at $T_{\alpha\gamma}$, this should give rise to a large drop in Θ_D resulting in the observed jump in the resistivity at the transition. Neutron diffraction studies could verify this suggestion. An anomaly in the elastic properties may also be observed because of the possible coupling between the soft optical and acoustical modes at $T_{\alpha\gamma}$. It is also noted that any changes in the crystal dimensions at $T_{\alpha\gamma}$ should also be taken into account for a quantitative analysis of the data.[5] However, such measurements in FeCo are lacking at present.

C. Region near 800 °K

In the nearly equiatomic FeCo alloys, an additional anomaly in the resistivity near 800 °K has been reported.[14] This anomaly is a function of the temperature of annealing and duration of annealing. Using our sample annealed in a manner described in Sec. II, we measured ρ at $\frac{1}{2}$ °C steps in the temperature region near 800 °K. As shown in Fig. 1, no indication of an anomaly in the resistivity is seen in this temperature range.

IV. CONCLUDING REMARKS

Experimental evidence, using electrical-resistivity measurements, has been presented for the order-disorder and α-γ transitions in FeCo system. It is found that near the order-disorder transition the specific heat $C(T)$, within the experimental errors, is proportional to $\partial\rho/\partial T$. This agrees with a similar observation in β-brass. At the α-γ transition in FeCo, the observation of a large hysteresis accompanied by a sudden change in the electrical resistivity suggest this to be a first-order transition. Additional work in thermal expansion, elastic constants, neutron scattering, Mössbauer measurements, etc., near $T_{\alpha\gamma}$ is needed to provide further insight into the nature and mechanism responsible for the α-γ transition.

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[9]The values of $\partial\rho/\partial T$ shown in Figs. 3 and 4 represent a 35-point fit to a second-order polynomial except near T_c, where a 15-point fit is used for better resolution of the peak. The maximum in $\partial\rho/\partial T$ occurs at T_c = 1005.7 °K, the value used in our calculations of T/T_c for $\partial\rho/\partial T$ in Fig. 4. This value of T_c differs from that derived from the specific-heat maximum by Orehotsky and Schröder (T_c = 995 °K) for a stoichiometric FeCo. However, we believe this should have no effect on the major conclusions drawn from Fig. 4, since OD transformation in FeCo is known to occur over a large composition range.

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