

Effect of pressure on magnetic transformations in an iron-rhodium alloy

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The effect of pressure on the Curie point T_C and the phase transition temperature T_0 from the antiferromagnetic to the ferromagnetic state is investigated for an equiatomic iron-rhodium alloy. The T - P phase diagram of the alloy is plotted for pressures up to 120 kbar and temperatures up to 700°K. Both T_0 and T_C vary linearly with the pressure at pressures up to 30 kbar, the slopes being $dT_0/dP = 4.7$ deg/kbar and $dT_C/dP = -1$ deg/kbar. The slopes dT_0/dP and dT_C/dP tend toward zero as the pressure increases further. The triple point at which the antiferromagnetic, ferromagnetic, and paramagnetic phases coexist lies at a pressure between 75 and 80 kbar. At pressures above 80 kbar the alloy passes directly from the antiferromagnetic to the paramagnetic state by a first-order phase transition whose transition temperature is independent of pressure.

1. INTRODUCTION

It has been found^[1-3] that the magnetization of an iron-rhodium alloy of near equiatomic composition changes sharply when the specimen is heated above a certain temperature T_0 that depends on the composition. Kouvel and Hartelins^[3] measured the magnetization of an Fe-Rh alloy containing 52 at. % Rh in a 5 kOe field at temperatures from 77 to 770°K; they found $T_0 = 350^\circ$ K and $T_C = 675^\circ$ K (Curie point).

X-ray^[4] and neutron-diffraction^[5] studies have shown that a phase transition from the antiferromagnetic to the ferromagnetic state takes place at T_0 and that the alloy has an ordered bcc structure of the CsCl type both above and below the transition temperature. It has also been found that T_0 depends strongly on the magnetic field strength^[6] and on the hydrostatic pressure^[6-11].

The first investigation of the effect of temperature on the magnetic transition points T_0 and T_C were reported in^[7]. It was found that the temperature range within which the FM phase⁽¹⁾ exists becomes narrower as the pressure increases, and that the $T_0(P)$ and $T_C(P)$ curves may intersect in a triple point at $P \approx 50$ kbar. At pressures above 50 kbar the AFM phase should pass directly to the PM phase at the Néel point T_N . We thought that the addition of a small quantity of iridium to the alloy might reduce this pressure; such addition greatly reduces the region in which the PM phase exists^[12].

In^[7], attention was called to the interesting features of the T - P diagram for rhodium alloys, and a number of papers on this topic appeared in a comparatively short time. The effect of pressure on T_0 and T_C for ternary alloys was investigated in^[8,10,11], and the authors thought that they had found triple points. Leger et al.^[10] report that the AFM-PM transition is a first order phase transition and that $dT_0/dP = dT_N/dP$ at the triple point. Vinokurova^[11] says that this is a second order phase transition and that dT_0/dP and dT_N/dP are not equal at the triple point. The specimens used in these two studies were close in composition. Thus, the data in the literature on the T - P diagram of iron-rhodium alloys are contradictory.

We have continued our study of the T - P diagram of an equiatomic iron-rhodium alloy; the results of this work are presented here.

2. EXPERIMENTAL RESULTS

The measurements were made on the same equiatomic specimens as were investigated previously^[6,7]. A two-stage piston-type pressure chamber, calibrated against the phase transitions in bismuth at 25.5 kbar and thallium at 37.6 kbar, was used for pressures up to 60 kbar. Pressures above 60 kbar were produced in Bridgman anvils with conical supporting pieces and external heating. This chamber was calibrated against the phase transitions in bismuth at 25.5 and 77 kbar and in iron at 126 kbar. The pressure in the piston-type chamber was measured within ± 1 kbar, and that in the anvils, within ± 2.5 kbar. Up to six electrical leads could be brought into the high pressure regions of both chambers.

Curves showing the temperature dependence of the electrical resistivity ρ of the FeRh specimens as measured at various pressures in the piston-type chamber are presented in Fig. 1. These curves have the

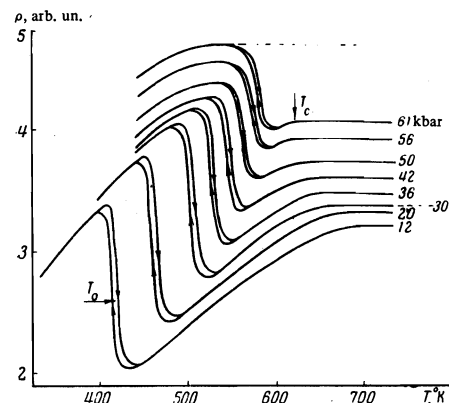


FIG. 1. Electrical conductivity of an iron-rhodium alloy vs temperature at various pressures. (The pressures were produced in the piston-type chamber.)

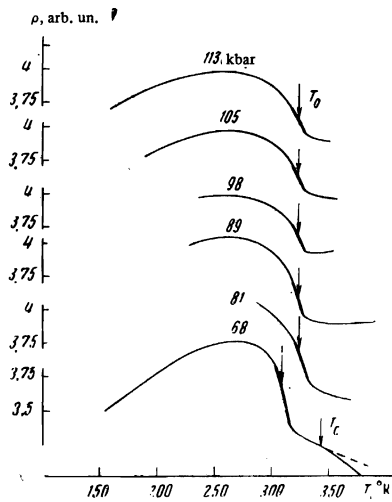


FIG. 2. Electrical conductivity of an iron-rhodium alloy vs temperature at various pressures. (The pressures were produced in Bridgman anvils.)

same general trend as the curve obtained by Kouvel and Hartelins at atmospheric pressure^[3]. The resistivity first increases with increasing temperature, and then falls suddenly at a certain temperature T_0 . Neutron-diffraction^[5] and magnetic^[1-3,6] measurements show that at this temperature there is a first order phase transition from the AFM to the FM state. We have previously measured the volume change in the AFM-FM transition^[7] and found it to be $\Delta V/V = (0.75 \pm 0.03) \cdot 10^{-2}$. In the FM state, ρ resumes its increase with increasing temperature, the curve having a flex at the Curie point. The equilibrium temperature T_0 for the AFM and FM phases was taken as the average of the transition temperatures measured on heating and cooling the specimen.

At low temperatures the AFM-FM transition is sharp, ρ continuing to increase until the phase transition begins. At high pressures ($P > 40$ kbar) there is a section of the $\rho(T)$ curve in the AFM region near the AFM-FM transition in which ρ is almost independent of temperature. The change $\Delta\rho$ in ρ at the AFM-FM transition decreases with increasing pressure and amounts to $0.35 \Delta\rho_0$ at $P \approx 60$ kbar, where $\Delta\rho_0$ is the change in ρ at $P = 0$ (Fig. 1). The hysteresis in the transition amounts to 7° at $P = 0$ and tends to zero as the pressure rises.

The results of measuring ρ in the Bridgman anvils are shown in Fig. 2. The curves have the same general trend as those in Fig. 1. The linear section corresponding to the AFM-FM transition at T_0 is readily seen on the $\rho(T)$ curve measured at 68 kbar. As the temperature is increased further there appears a flex, corresponding to the Curie point.

The decrease in ρ with increasing temperature above T_0 is an instrumental effect associated with the Bridgman anvils. It is observed during the first heating-cooling cycles after the pressure is stabilized but is no longer observed after repeated cycles (e.g., at $P = 98$ kbar). The linear sections of the $\rho(T)$ curves corresponding to a first order phase transition at T_0 are still fairly evident at 61 and 81 kbar. With further increase of the pressure, the $\rho(T)$ curve tends to become smoother. The sections of the $\rho(T)$ curves that correspond to the first order phase transition in the investigated pressure interval are drawn heavy in Fig. 2. The experimental fact that the $\rho(T)$ curve becomes smoother at pressures

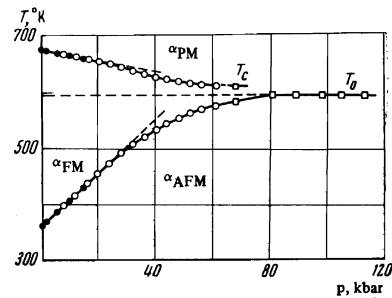


FIG. 3. T-P phase diagram for an iron-rhodium alloy. The black circles represent data from [7] obtained under hydrostatic pressure.

of 81 kbar and higher does not exclude the possibility that the phase transition at T_0 may become a first order transition at higher pressures.

We observed no temperature hysteresis in the transition at pressures above 68 kbar; if there is such hysteresis it cannot exceed 1.5°C .

The flex on the $\rho(T)$ curve corresponding to the Curie point, which is observed at pressures of 68 kbar and lower, does not appear at pressures of 81 kbar and higher (Figs. 1 and 2). In all probability the first order phase transition at pressures of 81 kbar and higher is the transition from the AFM state to the PM state.

The P-T diagram for the FeRh alloy shown in Fig. 3 was plotted from the experimental data on the $\rho(T)$ curves. This diagram can be separated into three parts:

$$P < 28 \text{ kbar}, \quad 28 < P < 80 \text{ kbar}, \quad P > 80 \text{ kbar}.$$

In the $P < 28$ kbar region both T_0 (the AFM-FM transition temperature) and T_C (the Curie point) depend linearly on P , the gradients being $dT_0/dP = 4.7 \pm 0.1$ deg/kbar and $dT_C/dP = -0.9 \pm 0.1$ deg/kbar. Both dT_C/dP and dT_0/dP tend toward zero in the $28 < P < 80$ kbar region, and T_0 is independent of P at $P > 80$ kbar.

3. DISCUSSION

The following arguments can be adduced in favor of the hypothesis that the phase transition at pressures of 81 kbar and higher is a first order transition from the AFM state to the PM state:

It is evident from Fig. 1 that the temperature interval in which the FM phase exists at ~ 60 kbar is very narrow, being only some 40° wide, while the change $\Delta\rho$ in the resistivity at the AFM-FM transition is still quite large ($\sim 30\%$ of its value at atmospheric pressure). In view of the weak temperature dependence of ρ in the FM phase and the narrow temperature range in which that phase exists, we may suppose that $\Delta\rho$ is the difference between the values of ρ in the AFM and PM phases. That would mean that the AFM-PM phase transition must be of the first order.

The temperature T_0 of the AFM-PM phase transition is independent of pressure at $P > 80$ kbar (Fig. 3). According to Clapeyron's equation, this means that $\Delta V = 0$. Thus, the AFM-PM phase transition is accompanied by a considerable change in ρ and no volume change. In all probability, the fairly large change in ρ with a zero volume change means that the AFM-PM transformation involves a change in the band structure of the alloy, and that is just the condition for a first order phase transition. The FM-PM transition is of the second order and

does not involve a change in the band structure. In this case, therefore, the FM and AFM phases will differ not only in the orientations of the magnetic moments of the iron sublattices, but also in the band structure.

First order magnetic phase transitions have been found in a number of substances. The most complete collection of data on this topic will be found in the review article by Grazhdankina^[13]. As a rule, these phase transitions are accompanied by large volume changes. This experimental fact is reflected in Kittel's theory of order-order transitions^[14] and in Bean and Rodbell's theory of order-disorder transitions^[15]. In both theories, first order magnetic phase transitions are attributed to a strong dependence of the exchange interaction on the interatomic distance, and that accounts for the considerable pressure coefficient of the transition temperature.

The AFM-FM transition in the iron-rhodium alloy at low pressures is accompanied by a considerable volume change ($\Delta V/V = 0.75\%$) and a strong pressure dependence of the transition temperature T_0 ($dT_0/dP = 4.7$ deg/kbar). It might seem that this phase transition could be attributed to a strong dependence of the exchange interaction on the interatomic distance. However, the experiments at higher pressures, beginning at $P \geq 80$ kbar, show that $\Delta V \approx 0$ and $dT_0/dP = 0$ in the AFM-FM and AFM-PM transitions. Hence neither Kittel's nor Bean and Rodbell's theory can account for the magnetic transformations in the iron-rhodium alloy. This example shows that any explanations of first order magnetic phase transitions in metals and alloys that is based on the assumption of a strong dependence of the exchange interaction on the interatomic distance must be approached with caution.

In the following we shall consider the part played by the rhodium ions in the AFM-FM transformations in an attempt to account for the phase diagram shown in Fig. 3.

In ordered iron-rhodium alloys with rhodium concentrations below 50 at.% the iron ions occupy the vertices of the bcc cell (Fe_I position) and positions in the center at rhodium sites (Fe_{II} position)^[5]. Shirane et al.^[5] made a neutron-diffraction study of iron-rhodium alloys over a wide range of composition and found the following atomic magnetic moments in the ferromagnetic region at 298° K for alloys with Rh concentrations of 35, 40, and 48 at.%:

$$\mu_{FeI} = 3.1 \mu_B, \quad \mu_{FeII} = 2.5 \mu_B, \quad \mu_{Rh} = 1.0 \mu_B.$$

In the alloy with 50 at.% Rh, which is antiferromagnetic at 298° K, $\mu_{FeI} = 3.3 \mu_B$, i.e., it is somewhat larger than in the ferromagnetic phase. It was also noted in^[5] that μ_{Rh} is considerably smaller than $1 \mu_B$ in the AFM region

From estimates of the lattice contribution to the total entropy change in the AFM-FM transformation in conjunction with measurements of the magnetic susceptibility in the AFM region, Kouvel^[12] concluded that the rhodium ions have no localized magnetic moment in the AFM region. In the FM state, the iron sublattice produces a fairly strong effective field at the rhodium sites, which induces a magnetic moment in the rhodium ions. The authors of^[16,17] suggest that the magnetic moments at the rhodium ions in the FM state are produced by a system of collectivized electrons: the resultant magnetic moment of the iron sublattice splits the rhodium d subband, and this leads to the appearance of a magnetic moment at the rhodium ions.

Let us make some rough estimates of the pressure dependence of the magnetization in iron-rhodium alloys, which we shall need in order to explain the behavior of the $T_0(P)$ and $T_C(P)$ curves.

Kouvel^[12] made a detailed study of the effect of dopants such as palladium, platinum, and iridium on T_0 , T_C , and the saturation magnetization σ_S for near equiatomic iron-rhodium alloys. The dopants affect T_0 and σ_S much as does high pressure. For example, Kouvel found that $T_C = 668^\circ$ K and $\Delta\sigma(\text{AFM-FM}) = 115$ cgs-emu/g for the alloy $\text{FeRh}_{1.08}$, while for the ternary alloy $\text{FeRh}_{1.08}\text{Pt}_{0.056}$ he found $T_C = 636^\circ$ K and $\Delta\sigma(\text{AFM-FM}) = 105$ cgs-emu/g. Thus, adding the platinum reduced T_C by 32° , whereas raising the pressure to ~ 30 kbar would reduce T_C by the same amount (the results of many studies have shown that $dT_C/dP \approx 0.9-1.1$ deg/kbar for near equiatomic alloys). From these data we can estimate the effect of pressure on the magnetization of the alloys at the AFM-FM transition temperature; we find $d\sigma_S/\sigma_S dP \approx -0.31 \cdot 10^{-2}$ kbar⁻¹. Now we can use this value to estimate the effect of pressure on σ_0 at 0° K. According to Kouvel and Wilson^[18] we have

$$\begin{aligned} \frac{1}{\sigma_0} \frac{d\sigma_0}{dP} &= \frac{1}{\sigma_0} \frac{d\sigma_s}{dP} + \frac{T_0}{T_c} \frac{1}{\sigma_0} \left(\frac{d\sigma_s}{dT} \right)_P \frac{dT_c}{dP} \\ &\approx -0.18 \cdot 10^{-2} \text{ kbar}^{-1}. \end{aligned}$$

From Kouvel's work we know that $d\sigma_S/\sigma_S dT \approx -2.5 \cdot 10^{-3}$ deg⁻¹, and a typical value for dT_C/dP would be about -1 deg/kbar. These estimates show that the magnetization of iron-rhodium alloys should decrease with increasing pressure.

On extrapolating T_0 from the high-pressure region (the dashed line on Fig. 3) we obtain $T_0 = 500^\circ$ K at $P = 0$. At pressures above 80 kbar the PM and AFM phases have equal compressibilities and there is no volume change at the AFM-PM transition. If these properties should persist as the pressure is lowered, the AFM phase would pass directly into the PM state as the temperature is raised at $P = 0$. Actually, however, on reducing the pressure we observe the following behavior: an FM phase appears and the temperature range throughout which it exists widens rapidly; nonzero volume and compressibility changes appear at the FM-AFM transition^[7]; and the magnetization rises considerably. We are led to ask why these effects occur.

Let us assume that the magnetic moment of the iron sublattices does not change with pressure; support for this assumption can be found in the fact that $d\sigma_S/\sigma_S dP \approx -3 \cdot 10^{-4}$ kbar⁻¹ for pure iron^[19]. Neutron diffraction measurements^[5] indicate that the rhodium contributes 25% of the total magnetization. Let us attribute our roughly estimated change in the magnetization with pressure to changes in the magnetic moments of the rhodium ions, and let us assume that $d\sigma_0/dP$ is independent of pressure. Then raising the pressure to ~ 100 kbar will reduce σ_0 by about 25%. The estimates given above favor the hypothesis that the magnetic moments associated with the rhodium ions disappear under the action of high pressure.

We shall consider the magnetic moments associated with the rhodium ions from the point of view of electron-band magnetism, as was done in^[16,17]. In the FM phase at atmospheric pressure, the Rhodium d subbands are split by the field of the iron sublattice, and this leads to the "induced" magnetic moment μ_{Rh} and to the positive volume change at the AFM-FM transformation. In-

creasing the pressure hinders this process. That also explains why the ferromagnetic region narrows rapidly with increasing pressure; $\Delta V(\text{AFM-FM})$ tends to zero, and according to our estimates, the magnetization falls.

Direct measurements of the effect of pressure on the magnetization of iron-rhodium alloys at low temperatures, especially for alloys that retain the FM phase at 0° K but whose compositions are still close to equi-atomic, would be useful in connection with the estimates made above.

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¹⁾Throughout the paper we use the abbreviations AFM, FM, and PM for the antiferromagnetic, ferromagnetic, and paramagnetic phases, respectively.

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