INVESTIGATION OF THE ANTIFERRO-FERROMAGNETISM TRANSITION IN AN FeRh *ALLOY IN A PULSED MAGNETIC FIELD UP TO 300 kOe*

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The magnetization of an $Fe_{0.48}Rh_{0.52}$ alloy was measured in a pulsed magnetic field up to 300 kOe over the temperature interval 77 to 330°K. From the magnetization curves were found the temperature dependences of the difference of free energy $\Delta F(T)$ between the ferromagnetic and the antiferromagnetic states, of the critical field $H_c(T)$ for the transition, of the magnetization jump $\Delta\sigma$ in the transition, and of the entropy jump $\Delta S(T)$ in the transition. It is shown that $\Delta F(T)$ and $H_c(T)$ depend quadratically on the temperature; $\Delta\sigma$ is practically independent of temperature; and $\Delta S(T)$ depends linearly on the temperature. The results obtained are in agreement with the hypothesis that the transition is of electronic nature. On the basis of this hypothesis and of the experimental values of $H_c(T)$ and $\Delta F(T)$, the value of the change of the electronic heat coefficient in the transition is found to be $\Delta\gamma = (0.54 \text{ to } 0.59) \times 10^3$ erg/g deg^2; this agrees well with the results of low-temperature specific heat measurements by Tu et al. ($\Delta\gamma = 0.44 \times 10^3$ erg/g deg^2) and by Ivarrson et al. ($\Delta\gamma = 0.52 \times 10^3$ erg/g deg^2).

IN ordered FeRh alloys near the equiatomic composition, when the temperature is raised above T_c there occurs a transition from the antiferromagnetic to the ferromagnetic state (AF–FM transition); it is a phase transition of the first kind[1-4]. At $T < T_c$ this transition can be brought about in a field exceeding a critical value $H_c(T)$. The mechanism of this transition at present has no theoretical explanation. The exchange-interaction inversion theory of Kittel[5] and the four-sublattice model of McKinnon et al.[6] describe the transition only qualitatively.

On the basis of the results of measurements of critical field values near the transition temperature in FeRh alloys with small additions of Pd, Pt, and Ir[7], and also of measurements of the low-temperature heat capacity[8], Tu et al.[8] conjectured that the FM and AF states in the FeRh alloy differ chiefly with respect to the values of the density of states of the conduction electrons near the Fermi level; this leads to different values of the electronic heat coefficient, γ_{FM} and γ_{AF}, in the FM and AF states. This supposition leads to a linear temperature dependence of the entropy difference ΔS between the FM and AF states[8]:

$$\Delta S \approx \Delta S_{el} = \int_0^T \frac{\Delta C_{el}}{T} dT = \Delta\gamma T. \quad (1)$$

Here ΔC_{el} is the difference between the electronic specific heats in the FM and AF states, and $\Delta\gamma = \gamma_{FM} - \gamma_{AF}$. The difference between the free energies of the FM and AF states, $\Delta F(T)$, according to[8] depends quadratically on the temperature:

$$\Delta F(T) \approx \Delta U(0°\,K) - \int_0^T \Delta S\, dT \approx \Delta U(0°\,K) - \frac{1}{2}\Delta\gamma T^2. \quad (2)$$

Here $\Delta U(0°K) = U_{FM}(0°K) - U_{AF}(0°K) = \Delta F(0°K)$; $U_{FM}(0°K)$ and $U_{AF}(0°K)$ are the internal energies of the FM and AF states at $T = 0°K$. It is assumed that the contributions of the exchange and magnetoelastic interactions to $\Delta F(T) - \Delta U(0°K)$ are unimportant at $T < T_c$. When the temperature is raised above $T_c = [2\Delta U(0°K)/\Delta\gamma]^{1/2}$ in the absence of an external field, the free energy of the FM state becomes less than the energy of the AF state, and this produces an AF-FM transition at $T = T_c$.

It was found by Tu et al.[8] that $\Delta\gamma = \gamma_{FM} - \gamma_{AF} = 0.44 \cdot 10^3$ erg/g deg^2; γ_{FM} was measured on the alloy $Fe_{0.51}Rh_{0.49}$ (which is ferromagnetic at helium temperatures), γ_{AF} on the alloy $Fe_{0.49}Rh_{0.51}$ (which is antiferromagnetic at helium temperatures). This method of determining $\Delta\gamma$ assumes that the FM state of the alloy $Fe_{0.51}Rh_{0.49}$ is practically the same as the FM state of the alloy $Fe_{0.49}Rh_{0.51}$; this, in general, is not obvious. By a similar method, Ivarsson et al.[9] obtained $\Delta\gamma = 0.52 \times 10^3$ erg/g deg^2, in good agreement with the results of Tu et al.[8] In[9], however, attention was paid to the very strong dependence of the value of γ_{AF} on composition. This situation compels one to treat the above-mentioned results with caution. In this connection it is useful to investigate the AF-FM transition in an FeRh alloy of a single definite composition by measurements of the magnetization in a magnetic field above the critical value, over a quite wide temperature interval ($T < T_c$).

The value of $\Delta F(T)$, which is equal to the work expended by the magnetic field in producing the AF-FM transition, is determined by graphical integration of the experimental magnetization curves at various temperatures:

$$\Delta F(T) = \int_0^{\sigma_S} H\, d\sigma. \quad (3)$$

If the conjecture of Tu et al.[8] is correct, then the temperature dependence $\Delta F(T)$ found in this manner should be described by the relation (2), with a coefficient $\Delta\gamma$ close to the value from[8,9] given above. If the magnetization jump $\Delta\sigma$ in the AF-FM transition is independent of temperature, then, on the basis of what was presented above, it can be shown that the temperature dependence of the critical field is described by the relation

$$H_c(T) = H_\kappa(0^\circ \mathrm{K}) - \frac{1}{2}\frac{\Delta\gamma}{\Delta\sigma}T^2, \quad (4)$$

from which it is also possible to find $\Delta\gamma$ on the basis of the experimental values of $H_c(T)$.

The temperature dependence of the critical field for the AF-FM transition in FeRh alloy in the temperature interval 77 to 400°K has been investigated by a number of authors[6,10]. Zavadskiĭ and Fakidov[10] obtained a linear dependence $H_c(T)$, McKinnon et al.[6] a quadratic; the magnetization measurements in[6] were made only near room temperature, and an alloy far from the stoichiometric ($Fe_{0.388}Rh_{0.612}$). Because of the lack of measurements of the magnetization jump $\Delta\sigma$ in a large part of the temperature interval investigated, the verification of the hypothesis about the electronic character of the transition on the basis of the results of McKinnon et al.[6] is uncertain. For this reason, the research being reported was conducted.

We measured the magnetization of an $Fe_{0.48}Rh_{0.52}$ alloy in a pulsed magnetic field of intensity up to 300 kOe, duration 0.01 sec, in the temperature interval from 77 to 330°K. The experimental setup used in this research enabled us to photograph the magnetization curves on an oscillograph screen. The magnetization measurements were made by the induction method[11]. The errors of measurements of the magnetization and of the magnetic field were, respectively, 10 and 7%. The random errors (scatter of the experimental values) were for the critical field 2 to 3%, for the magnetization ~5%, The heat treatment of the specimen of FeRh alloy was similar to that used by Zakharov et al.[4] The measurements were made during lowering of the temperature.

Figure 1 shows some of the magnetization curves obtained. The sections of the curves with an abrupt rise of magnetization correspond to the Af-FM transition. The values corresponding to the maximum slope of the magnetization curves were taken as the critical field values H_c. The susceptibility in the AF state ($H < H_c(T)$) is $\chi_{AF} \approx 0.8 \times 10^{-4}$ emu/g and is practically independent of temperature far from T_c. The susceptibility in the FM state does not exceed 10^{-5} emu/g. The saturation magnetization σ_S at T = 77°K is 128 emu/g. The change of magnetization $\Delta\sigma$ in the AF-FM transition was determined as the distance between the envelopes of the family of magnetization curves (the dotted lines in Fig. 1). Within the temperature interval investigated, $\Delta\sigma$ = emu/g and is independent of temperature within the limits of random error (~50%). The results enumerated agree with the results of Zavadskiĭ and Fakidov[10]. The temperature depend-

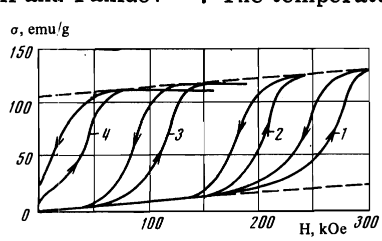

FIG. 1. Magnetization curves of $Fe_{0.48}Rh_{0.52}$ alloy: 1, 77°K; 2, 185°K; 3, 270°K; 4, 333°K.

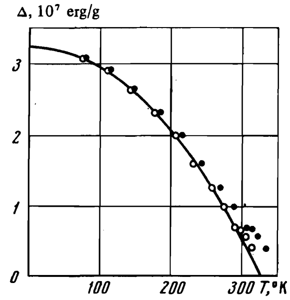

FIG. 2. Temperature dependence of the difference of free energy between the ferro- and antiferromagnetic states in $Fe_{0.48}Rh_{0.52}$ alloy. ●, without allowance for the magnetocaloric effect. O, with allowance for the magnetocaloric effect. The curve was calculated from the relation (2) with parameters $\Delta U(0^\circ K) = \Delta F(0^\circ K) = 3.23 \cdot 10^7$ erg/g, $\Delta\gamma = 0.59 \cdot 10^3$ erg/g deg², T_c = 331°K.

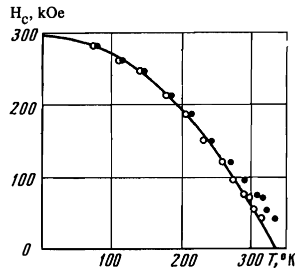

FIG. 3. Temperature dependence of the critical field for the transition in $Fe_{0.48}Rh_{0.52}$ alloy. O, without allowance for the magnetocaloric effect. O, with allowance for the magnetocaloric effect. The curve was calculated from the relation (4) with parameters H_c (0°K) = 297 kOe, $\Delta\gamma = 0.54 \cdot 10^3$ erg/g deg², T_c = 338°K.

ence of the critical field confirms the results of McKinnon[6].

In analyzing the experimental $\Delta F(T)$ and $H_c(T)$ curves measured in a pulsed field, it is necessary to take account of the change of temperature of the specimen in the AF-FM transition because of the magnetocaloric effect. Calculation of the heat exchange of the specimen with the surrounding medium[12] shows that under the conditions of this research, the AF-FM transition process is very close to adiabatic, and the change of temperature of the specimen because of the magnetocaloric effect in the AF-FM transition is described by the relation

$$(\Delta T)_S = -T(\Delta S)_T / C_H \quad (5)$$

with an error no greater than 5%. The value of $(\Delta S)_T$ were found from the relation

$$(\Delta S)_T = -\Delta\sigma dH_c / dT. \quad (6)$$

The specific heat C_H was determined according to a Debye curve. We estimated the Debye temperature for FeRh alloy as Θ_D = (300 ± 100)°K according to the low-temperature specific-heat curve given by Ivarsson et al.[9] The value of the magnetocaloric effect $(\Delta T)_S$, found thus from (5) and (6), amounts to −(20 ± 2)°K at T = 333°K and −(2 ± 1)°K at T = 77°K; the error in the values of $(\Delta T)_S$ is caused by the error in Θ_D. Thus in the calculation of the magnetocaloric effect the value of the specimen temperature incurs an error of 1%. The error of temperature measurement is 1%. Hence the total error in the value of the temperature is 2%. It should be remarked that within the limits of the indicated error, the same values of specimen temperature result from calculation of the magnetocaloric effect with C_H = 6 cal/g deg. Since the magnetocaloric effect was not taken into account in the papers of other authors[4,6,10], it must be supposed that the values of critical temperatures obtained there are too high by about 20°K.

Figures 2 and 3 shows the experimental values of $\Delta F(T)$ and $H_c(T)$, respectively. The dark points represent the results without allowance for the magnetocaloric effect at the transition; the light points were obtained by taking the magnetocaloric effect into account. The curve in Fig. 2 was calculated by formula (2) with the parameters $\Delta U(0^\circ K) = 3.23 \times 10^7$ erg/g, $\Delta\gamma = 0.59 \times 10^3$ erg/g deg^2, $T_C = 331^\circ K$; the curve in Fig. 3 was calculated by formula (4) with the parameters $H_C(0^\circ K) = 2.97 \times 10^5$ Oe, $\Delta\gamma = 0.54 \times 10^3$ erg/g deg^2, $T_C = 338^\circ K$. The values of $\Delta\gamma$ are close to those obtained by other authors[8,9], and the calculated curves describe well the experimental temperature dependences $\Delta F(T)$ and $H_C(T)$. From the relation (4) with $\Delta\gamma = 0.54 \times 10^3$ erg/g deg^2 and $\Delta\sigma = 104$ emu/g, the value of the derivative of the critical field with respect to temperature was found at $T = T_C$ ($dH_C/dT = -1.75$ kOe/deg). The value of the entropy jump ΔS can be found either from (1), or from (6) by use of the known value of dH_C/dT. At $T = T_C$, the value obtained is $\Delta S = 1.83 \times 10^5$ erg/g deg. The latent heat of the transition is $T_C\Delta S = 6.2 \times 10^7$ erg/g. Zakharov et al.[4] obtained $dH_C/dT = -1.7$ kOe/deg, $\Delta S = 1.92 \times 10^5$ erg/g deg, and $T_C\Delta S = 6.7 \times 10^7$ erg/g. Here a correction must be made for the magnetocaloric effect; this leads in this case to an increase of the absolute values by about 15 to 20%. Thus the agreement with the results of[4] is completely satisfactory. McKinnon et al.[6] obtained, for the $Fe_{0.469}Rh_{0.531}$ alloy at $T = T_C$, $\Delta S = 0.87 \times 10^5$ erg/g deg; this is smaller by a factor of almost 2 than the corresponding values obtained in the present research and by Zakharov et al.[4] This value was obtained from model concepts set forth in[6], which give a rather crude description of the AF-FM transition mechanism in an FeRh alloy. An estimate made by means of the usual thermodynamic relation (6), with use of the experimental value of dH_C/dT from[6] and of values of $\Delta\sigma$ from[4,10] or from the present research, with allowance for the magnetocaloric effect, at $T = T_C$, gives $\Delta S = (1.7$ to $1.8) \times 10^5$ erg/g deg, which agrees well with the results of the present work.

In order to estimate the departure of the exponent in the experimental temperature dependences $\Delta F(T)$ and $H_C(T)$ from 2, it is convenient to plot these dependences on a logarithmic scale. On noting that $T_C = (2\Delta U(0^\circ K)/\Delta\gamma)^{1/2}$ and taking logarithms in (2) and (4), we get

$$\ln [1 - \Delta F(T) / \Delta F(0^\circ K)] = 2 \ln (T / T_c); \tag{7}$$

$$\ln [1 - H_c(T) / H_c(0^\circ K)] = 2 \ln (T / T_c); \tag{8}$$

Figure 4 shows the experimental dependence of the quantities on the left side of (7) (dark points) and (8) (light points) on the value of $\ln(T/T_C)$. It is seen that the experimental points fall close to the straight line of slope 2. The error in determination of the value of the slope, found from the experimental scatter of the points in Fig. 4, does not exceed ±0.2. For comparison, straight lines of slopes $3/2$ and $5/2$ are plotted in Fig. 4; these correspond to $T^{3/2}$ and $T^{5/2}$ laws. It is seen that the experimental error allows a sure separation of a T^2 law from a $T^{3/2}$ or a $T^{5/2}$.

From what has been set forth above, it follows that the experimental temperature dependences $\Delta F(T)$ and $H_C(T)$ can be represented in the forms (2) and (4) respectively, the exponent of T being 2.0 ± 0.2 and the value of $\Delta\gamma$ being close to that obtained by other authors[8,9]. The results obtained give evidence in

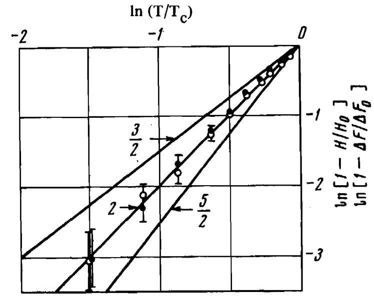

FIG. 4. Reduced temperature dependences of the critical field (O) and of the difference of free energy between the ferro- and antiferromagnetic states (●), plotted on a logarithmic scale. $T_C = 338^\circ K$. The numbers on the graph indicate the slopes of the corresponding straight lines and are equal to the exponents n in a temperature-dependence law of the form $1 - H/H_0 = (T/T_C)^n$.

favor of the hypothesis of the electronic nature of the AF-FM transition in the FeRh alloy[8]. McKinnon et al.[6] reach the same conclusion by analyzing the dependence of the critical field on temperature and on lattice parameter, within the framework of their four-sublattice model. As was indicated above, however, this theory is a rather crude approximation, as was indeed remarked by the authors themselves. Kittel's mechanism of exchange-interaction inversion[5], as was shown in[6], gives results differing by an order of magnitude from the results of experiment and cannot explain the antiferro-ferromagnetism transition in the FeRh alloy.

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