MAGNETIC AND MAGNETOELASTIC PROPERTIES OF A METAMAGNETIC IRON-RHODIUM ALLOY

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The temperature dependence of magnetization, magnetostriction, Young's modulus, and the crystal-lattice parameter is investigated in an FeRh alloy in which, at a certain temperature T_k, a transition from a ferromagnetic to an antiferromagnetic state occurs. A sudden change in the temperature behavior of the properties mentioned is observed near T_k. The influence of a magnetic field (up to 140 kOe) and of hydrostatic pressure (up to 25 katm) upon the transition temperature is studied. The results obtained are compared with Kittel's phenomenological theory.

INTRODUCTION

MAGNETIC[1-5] and neutron-diffraction[5-6] investigations of ordered alloys of the system FeRh, near the equiatomic composition $Fe_{0.5}Rh_{0.5}$, have shown that in these alloys, which are ferromagnetic at high temperatures, a transition to an antiferromagnetic state occurs upon cooling to a certain critical temperature T_k. Both above and below the transition point, the alloys have an ordered body-centered cubic structure of CsCl type; but on cooling below T_k, the lattice parameter decreases discontinuously by about 0.2%[6]. In the ferromagnetic state a magnetic moment is observed both on the iron atom (3 μ_B) and on the rhodium atom ($\sim 0.8\ \mu_B$), with the magnetic moments of the iron and rhodium atoms parallel[5]. Below T_k the magnetic moments of the iron atoms form an antiferromagnetic structure, in which each iron atom is surrounded by six other iron atoms with oppositely oriented magnetic moments[5]; there are no data on the magnitude and orientation of the magnetic moments of the rhodium atoms at $T < T_k$.

The information that exists at present is insufficient for explanation of the nature and type of the antiferromagnetism-ferromagnetism transition in this interesting material. In the phenomenological theory of Kittel[7], such a transition is explained by a dependence of the exchange-interaction integral on the crystal-lattice parameter. The basic assumption of this theory is the following: the exchange-interaction integral depends linearly on the lattice parameter and changes sign at a certain critical value of that parameter. If, because of thermal expansion, the lattice parameter reaches the critical value at a certain temperature T_k, a transition from the ferro- to the antiferromagnetic state occurs. However, a comparison of experimental data on FeRh alloys with this theory has not yet been made, for the properties of these alloys are very sensitive to composition (the ferromagnetism-antiferromagnetism transition temperature T_k increases by 230°K on change of the rhodium content from 50 to 55 atomic percent[1]), and therefore it is difficult to compare with each other the results of measurements of diferent physical properties made on different specimens.

In the present work, various magnetic, magnetoelastic, and structural properties of an FeRh alloy near the critical temperature T_k were investigated on specimens of a single melt, subjected to identical heat treatments; this permitted a comparison of the results of the different measurements with each other and a comparison of the data obtained with the theory of Kittel.

The FeRh alloy was melted in a high-frequency furnace in a vacuum. Then the alloy was annealed at 1100°C for five hours and was cooled in the furnace. For a check of the influence of heat treatment on the properties of the alloy, some measurements were also taken on an alloy hardened by quenching in water (from temperature 1100°C).

MAGNETIC PROPERTIES

Measurements of the magnetization of the annealed alloy in fields up to 2000 Oe were made in a solenoid by a ballistic method; they showed that at room temperature the alloy is antiferromagnetic. The transition to a ferromagnetic state occurs in a

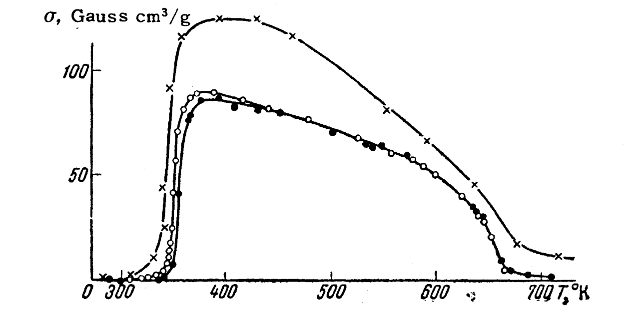

FIG. 1. Temperature dependence of magnetization of FeRh alloy at H = 1770 Oe (•, heating; o, cooling) and at H = 14,500 Oe (×, heating).

field 1770 Oe on heating to 358°K and on cooling to 352°K (Fig. 1). In the transition region, in a temperature interval from about 330 to about 440°K, thermal hysteresis is observed; this indicates the presence of a broad transition range near T_k. The "smearing" of the transition with respect to temperature is caused, apparently, by some nonuniformity of the alloy; it can also be a consequence of the action of internal elastic stresses. The Curie point Θ of the alloy, determined from the temperature behavior of the magnetization in a weak field of 9 Oe, is approximately 660°K. Measurements taken by the ballistic method in a magnet showed also that the transition temperature decreases by approximately 12° on increase of the field to 14,500 Oe (Fig. 1).

For a more complete investigation of the influence of a magnetic field on the temperature of transition from an antiferromagnetic to a ferromagnetic state, measurements of the magnetization were made in pulsed magnetic fields up to 140 kOe. The magnetization was determined by the ponderomotive method, from the force pulling the specimen into a nonuniform magnetic field [9]. The accuracy of the magnetization measurement was 10%. Figure 2 shows the magnetization isotherms at various temperatures. It is seen that

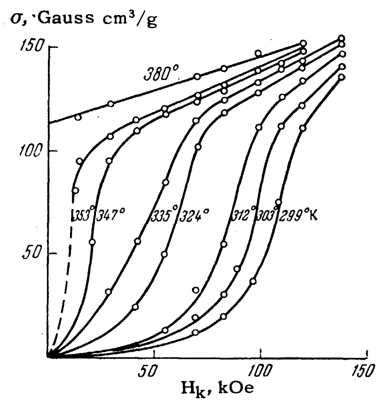

FIG. 2. Magnetization isotherms of FeRh alloy in pulsed magnetic fields.

below T_k, the magnetization increases suddenly on attainment of a certain field: under the influence of the field, a transition from an antiferro- to a ferromagnetic state occurs. This transition is somewhat "smeared out" with respect to field. We defined the critical field H_k as that value of the magnetic field at which the most rapid increase of magnetization occurs. It is seen from Fig. 2 that H_k decreases with increase of temperature. The dependence of the field on temperature is shown in Fig. 3. H_k depends linearly on temperature; the value of dH_k/dT is -1.7×10^3 oe/deg.

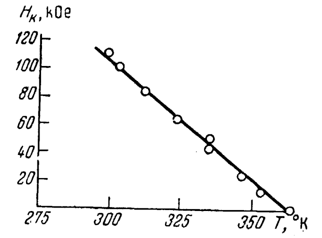

FIG. 3. Temperature dependence of critical field H_k of FeRh alloy. Curve taken on heating.

TEMPERATURE DEPENDENCE OF THE CRYSTAL-LATTICE PARAMETER

In agreement with the results of other authors, x-ray investigations showed that the annealed FeRh alloy has an ordered cubic structure of CsCl type, and that the transition at the point T_k is accompanied by a change of the lattice parameter of the alloy. The measurements were made on a diffractometer [10] over a wide temperature interval, including the antiferro-, ferro-, and paramagnetic regions. The radiation used was Mo K_α, filtered by a Zr foil 0.1 mm thick. The lattice parameter a was determined from several lines, for which the sums of the squares of the indices were 50, 54, 62, and 66, by extrapolation of a dependence $a = f(\cos^2 \varphi)$ to angle $\varphi = 90°$.

The dependence of the lattice parameter on temperature for the annealed alloy is shown in Fig. 4. On increase of temperature, the lattice parameter increases smoothly up to the temperature at which the transition of the alloy from an antiferromag-

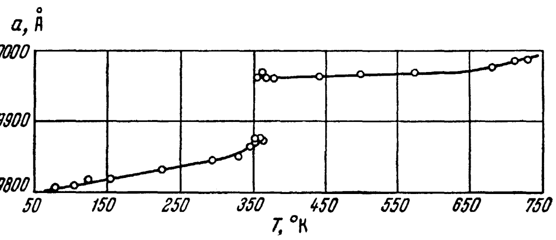

FIG. 4. Temperature dependence of crystal-lattice parameter of FeRh alloy. Curve taken on heating.

netic to a ferromagnetic state begins, at $T_k \approx 353°K$. At this temperature a new ferromagnetic phase forms: the lattice parameter suddenly increases by 0.3%. In the temperature interval from about 350 to about 440°K, remnants of the antiferromagnetic phase are observed along with the ferromagnetic phase.

In the two-phase region, tetragonal and rhombic distortions of the lattice are observed; these are apparently connected with the effect of elastic stresses, which originate because of the presence of two phases.

Above the Curie point ($\Theta = 660°K$), the lattice parameter increases with temperature faster than in the ferromagnetic region.

X-ray investigations of the quenched alloy showed that the degree of atomic ordering is only slightly decreased by such treatment. However, in the quenched material the starting point of the transformation on heating is 367°K, i.e., 14° higher than in the annealed alloy. In addition, the thermal hysteresis of the transformation amounts in this case to 14°, whereas for the annealed alloy the hysteresis amounted altogether to only 3°K.

On the annealed alloy, measurements of the thermal expansion were also made with a dilatometer of Strelkov's [11] design; these confirmed in a general way the results of the investigation of the crystal-lattice parameter. Figure 5 shows the dependence of the relative elongation of the material on temperature. At the point of transition from an antiferromagnetic to a ferromagnetic state, $T_k \approx 353°K$, a jump of the specimen length by about 0.3% is observed. Above this temperature, the curve rises smoothly up to the Curie point, $\Theta \approx 660°$, where it undergoes a break; thereafter it has a steeper slope.

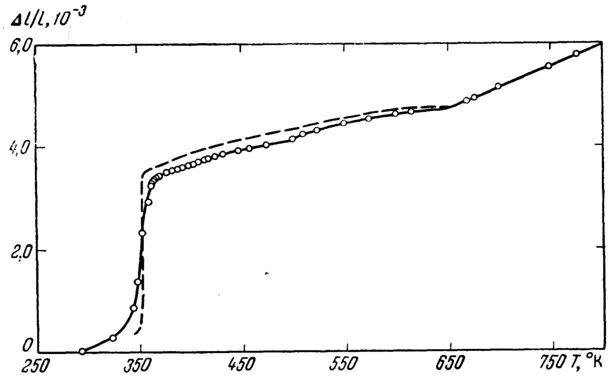

FIG. 5. Temperature dependence of thermal expansion of FeRh alloy. Solid line, experimental data taken on heating of the alloy; dashed line, calculation by formula (3).

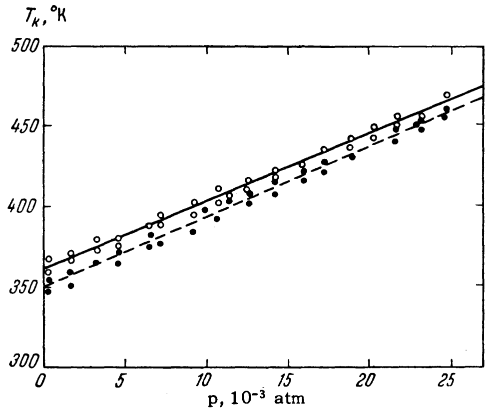

FIG. 6. Shift of transition temperature T_k of FeRh alloy by pressure: o – heating, • – cooling.

SHIFT OF THE ANTIFERROMAGNETIC-FERROMAGNETIC TRANSITION POINT BY HYDROSTATIC COMPRESSION

The effect of hydrostatic pressure on the temperature T_k in the FeRh alloy was studied by the method of thermal analysis in a high-pressure multiplier described earlier [12]. Isopentane served as the pressure-transmitting medium. The pressure was measured with a manganin manometer. Heating and cooling curves of the specimen were registered with a Kurnakov pyrometer. On the basis of the experimental data thus obtained, the dependence of the critical temperature T_k of the alloy on pressure was plotted; it is shown in Fig. 6. The scattering of the points over a region of about 10° is connected with inaccuracy in determination of the transformation temperature in connection with the fact that the transformation takes place over a certain temperature interval. From Fig. 6 it is seen that there is a temperature hysteresis of the transformation, with a width of about 10° to 15°. The transformation temperatures on heating and on cooling increase with increase of pressure approximately linearly. The value of dT_k/dp is 4.33×10^{-3} deg/atm.

YOUNG'S MODULUS AND MAGNETOSTRICTION

For a more detailed investigation of the character of the ferromagnetism-antiferromagnetism transition, the temperature dependences of Young's modulus and of the magnetostriction of the annealed FeRh alloy were also investigated. Young's modulus was measured by the composite-bar method [8] at a frequency of about 110 kc/sec. The magnetostriction measurements were made by means of wire strain gauges at constant current. Figure 7 shows the dependence of Young's modulus of the FeRh alloy on temperature. It is seen that on transition from the antiferromagnetic to the fer-

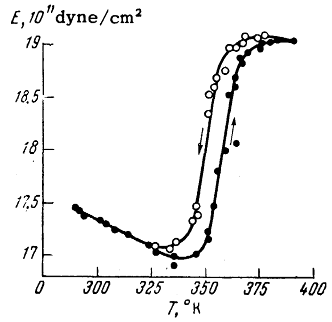

FIG. 7. Temperature dependence of Young's modulus of FeRh alloy: • – heating, o – cooling.

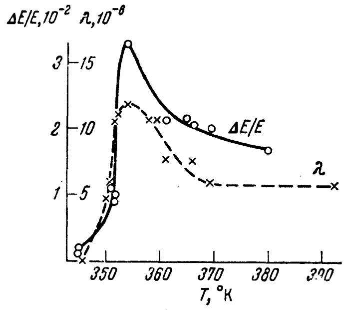

FIG. 8. Temperature dependence of magnetostriction (λ) and ΔE-effect (ΔE/E) of FeRh alloy in field 1770 Oe.

romagnetic state, the size of the modulus suddenly increases. In the T_k region, thermoelastic hysteresis is also observed.

Figure 8 shows the temperature dependence of the longitudinal magnetostriction λ and of the relative change of Young's modulus $\Delta E/E$ in a field of 1770 Oe. It is seen that λ and $\Delta E/E$ are equal to zero in the antiferromagnetic region and go through a maximum in the temperature region of the transformation. This maximum is apparently caused by the fact that in the transformation-temperature region, there are superposed on the usual ΔE-effect and magnetostriction, determined by domain processes, magnetoelastic effects connected with destruction of the antiferromagnetic structure under the influence of the field.

DISCUSSION OF THE MEASUREMENT RESULTS

Our measurements show, in agreement with the data of other authors [2-4], that the transition at temperature T_k in the FeRh alloy is a phase transition of the first kind; this is evidenced by the evolution of heat in the transition, the jump of the lattice parameter, the sudden change of magnetization in the transition region, and also the thermal hysteresis in the neighborhood of T_k. For a transition of the first kind, the Clapeyron-Clausius equations hold:

$$dT_k / dp = \Delta V / \Delta S, \qquad (1)$$

$$dH_k / dT = \Delta S / \Delta M, \qquad (2)$$

Here ΔV, ΔM, and ΔS are the discontinuities of volume, magnetization, and entropy in such a transition. By use of the relations (1) and (2), it is possible to determine from our experimental data, by two independent methods, the discontinuity of entropy in the ferromagnetism-antiferromagnetism phase transition in the FeRh alloy. The calculations give $\Delta S = (4.7 \pm 0.4) \times 10^{-3}$ cal/g deg by formula (1), $\Delta S = (4.6 \pm 0.4) \times 10^{-3}$ cal/g deg by formula (2).

Thus the size of the entropy discontinuity, as determined by the two methods, is the same within the limits of experimental error.

The heat of transformation from the antiferromagnetic to the ferromagnetic state for the FeRh alloy is equal to

$$H = T_k \Delta S = (1.6 \pm 0.2) \text{ cal/g}.$$

This value differs from the values obtained from magnetic measurements in [4] (H = 0.92 cal/g) and [3] (H ≈ 1 cal/g); this is apparently connected with the sensitivity of the properties of the alloy to composition and heat treatment.

At present there is no complete theory explaining the reason for the transition from the antiferromagnetic to the ferromagnetic state. As has already been mentioned, Kittel [7], to explain such a transition in the compound Mn_2Sb with added Cr, advanced the hypothesis that at the transition point a change of sign of the exchange interaction occurs, because of the strong dependence of the latter on the interatomic distance, which changes with change of temperature.

Kittel's theory was developed for a uniaxial layered magnetic structure; in the case of the FeRh alloy, which has cubic structure, it needs to be somewhat modified. For a cubic crystal we may suppose, as a first approximation, that the exchange interaction is isotropic and is dependent only on the volume of the elementary cell. If, following Kittel, we consider an antiferromagnetic with two magnetic sublattices, whose magnetizations $|\mathbf{M}_1| = |\mathbf{M}_2| = M$ are equal in absolute value and are oppositely directed, and if we suppose that the exchange interaction changes sign at a critical volume V_k of the elementary cell, it is easy to obtain an expression for the volume of the elementary cell in the ferromagnetic and antiferromagnetic regions:

$$V / V_T = 1 \pm \rho \varkappa_T M^2{}_T. \qquad (3)$$

Here V_T and κ_T are the volume of the elementary cell and the hydrostatic compressibility with neglect of the magnetic interaction (they can be obtained approximately by linear extrapolation from the paramagnetic region); M_T is the sublattice magnetization at temperature T; ρ is the derivative of the exchange-interaction parameter I with respect to volume deformation,

$$\rho = VdI / dV. \tag{4}$$

The plus sign in formula (3) refers to the ferromagnetic region, the minus sign to the antiferromagnetic. From formula (3) it follows that the discontinuity in volume at the point T_k, resulting from the transition from the antiferromagnetic to the ferromagnetic state, is

$$\Delta V / V_k = 2\rho\varkappa_k M^2{}_{T/k}. \tag{5}$$

From x-ray and magnetic data we find according to formula (5)

$$\rho\varkappa_k = 1.5 \cdot 10^{-8} \text{ G}^{-2}.$$

The quantity $\rho\kappa_k$ describes the rate of change of the parameter of exchange interaction between the sublattices with respect to hydrostatic pressure. As is known[13], this quantity, converted to a single atom, is equal to $kd\Theta/dp$, where Θ is the Curie temperature and k is Boltzmann's constant. By using the calculated value of $\rho\kappa_k$, we get for the FeRh alloy the value $d\Theta/dp \approx 5.7 \times 10^{-3}$ deg/atm. The value of the Curie-point shift for invar (cf.[14]) is -5×10^{-3} deg/atm. Thus we get for the FeRh alloy, from Kittel's theory, a reasonable value for the shift of Curie point with pressure.

By use of the calculated value of $\rho\kappa_k$, the temperature dependence of the magnetization, and the relation $\Delta V/V = 3\Delta l/l$, it is possible to plot from formula (3) the dependence of thermal expansion on temperature. This dependence is shown, dashed, in Fig. 5. Here V_T was extrapolated linearly from the paramagnetic region, and κ_T was assumed independent of temperature. It is evident that qualitative agreement of the experimental and the theoretically calculated values is observed. This is a confirmation of the applicability of Kittel's theory to the ferromagnetism-antiferromagnetism transition in the FeRh alloy.

From Kittel's theory it follows also that

$$\varkappa_k = \frac{1}{V_T}\frac{dV_T}{dT}\frac{dT_k}{dp}. \tag{6}$$

With this formula we find from our experimental data $\kappa_k = 1.1 \times 10^{-13}$ cm²/dyn.

For the majority of metals and alloys the hydrostatic compressibility is of order $(9 \text{ to } 3) \times 10^{-13}$ cm^2/dyn. Thus, for example, for Fe $\kappa = 5.94 \times 10^{-13}$ cm^2/dyn, for Rh $\kappa = 3.64 \times 10^{-13}$ cm^2/dyn[15]. For an FeRh alloy one would expect a value of the compressibility lying between these values, i.e., approximately 5×10^{-13} cm^2/dyn. The same order of magnitude is obtained if one calculates κ_T by using the experimental value of Young's modulus and taking the values of Poisson's ratio usual for metals, 0.25 to 0.35.

Thus we get from Kittel's theory a somewhat low value of the hydrostatic compressibility. The reason for such a discrepancy may lie in the approximate nature of the calculation. We considered an antiferromagnetic with two ferromagnetic sublattices. In reality it is necessary, in the FeRh alloy, to consider four sublattices: two "iron" and two "rhodium." The situation is further complicated by the fact that, as has already been mentioned, it is not known how the magnetic moment of the Rh atom behaves in the antiferromagnetic state; in the calculations, we assumed that its value does not change in the transition.

For final elucidation of the question of the applicability of Kittel's theory to the ferromagnetism-antiferromagnetism transition in the FeRh alloy, further investigations are necessary; and, in particular, it is necessary to determine the behavior of the magnetic moment of the Rh atom on transition to the antiferromagnetic state.

In closing, we consider it our pleasant duty to thank Prof. K. P. Belov for valuable counsel and S. A. Nikitin and É. I. Éstrin for fruitful discussions.

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