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MAGNETIC PROPERTIES OF TERNARY ALLOYS OF THE NICKLE-IRON-MANGANESE SYSTEM

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The saturation magnetization and temperature-dependence of the susceptibility of ternary Ni$(\mathrm{Fe}_y\mathrm{Mn}_{1-y})$ alloys is measured. It is shown that the magnetization goes to zero when the alloy contains 28 at.% Mn. Near the concentration $c_3^0 = 28$ at.% Mn, there is a region in which the magnetic properties have a strong field dependence. The results are discussed on the basis of the concept of disorientation of the atomic magnetic moments. This treatment enables us to conclude that the exchange interaction in Fe-Mn pairs is negative and that its magnitude is close to that of the exchange interaction in Mn-Mn pairs.

IN the present paper, magnetic properties of ternary alloys described by the formula Ni$(\mathrm{Fe}_y\mathrm{Mn}_{1-y})$ are investigated. The binary alloys NiFe and NiMn, the limiting compositions of our ternary alloys, are representative of two different forms of magnetic ordering. Permalloy of composition NiFe can be characterized as a ferromagnetic with a high Curie temperature (~500°C) and an appreciable mean magnetic moment per atom ($\sim 1.7\ \mu_B$)[1]. The 1 : 1 alloy NiMn is an antiferromagnetic with an orthorhombic magnetic unit cell formed by Mn atoms and a Néel temperature of the same order as the Curie temperature of the alloy NiFe[2]. It is necessary to note one essential feature of the atomic states of NiFe and NiMn. The above-mentioned characteristics of the magnetic state of the alloys refer to disordered NiFe and ordered NiMn. In fact, the alloy NiFe cannot be ordered by the usual heat treatment method and special measures are needed to obtain an ordered disposition of the atoms at the lattice sites[3]. In contrast to NiFe, the alloy NiMn is easily ordered and, evidently, it is difficult to obtain it in a disordered state. Thus, for constant nickel content (50 at.%) and a lattice of the nickel type, completely different magnetic structures are formed, depending on the nature of the second component.

Analyzing the behavior and properties of the most distinct alloys of the 3d-transition metals, we can observe the following regularity: in alloys formed by elements positioned to the right of chromium in the Mendeleev table, the magnetic moments of the components change insignificantly on large change of the composition; to describe these alloys it is convenient to use the concept of localized magnetic moments. The ternary alloys of nickel-iron-manganese can with complete justification be related to alloys of this type.

From the results of a large number of papers (we list only some of them[4-8]) in which the state and properties of the binary alloy systems Ni-Fe and Ni-Mn were studied, we can assume that the nature of the exchange interaction for pairs of atoms of these alloys is well established, namely $I_{\text{Ni-Ni}} > 0$, $I_{\text{Ni-Fe}} > 0$, $I_{\text{Fe-Fe}} < 0$ and $I_{\text{Mn-Mn}} < 0$. The negative exchange coupling for the Fe-Fe pair, being weak compared to the positive coupling for the Ni-Ni and Ni-Fe pairs, is not manifested in the composition (NiFe), in spite of the considerable number of Fe-Fe pairs in the alloy. The exchange interaction for the Mn-Mn pairs is stronger and has a noticeable effect on the magnitude of the magnetization in nickel-manganese alloys, beginning at a manganese content of about 7 at.%. In the 1 : 1 alloy NiMn the strong negative exchange interaction for the Mn-Mn pairs not only produces the antiferromagnetic structure of the alloy but, possibly, also facilitates the atomic ordering to some extent. The ternary nickel-iron-manganese alloys studied by us have a face-centered cubic lattice with parameters close in magnitude to those of the lattices of the γ phases of the alloys Ni-Fe and Ni-Mn. Therefore, it is natural to suppose that the magnitudes of the atomic magnetic moments and the signs of the exchange integrals of the pair interactions in these alloys are the same as in the binary alloys Ni-Fe and Ni-Mn. But in the ternary alloys there appears a new combination, absent in binary alloys, of nearest neighbors, the Fe-Mn pairs. The results of the magnetic measurements allow us to asses the nature of the exchange coupling in such pairs. Apart from this, the data from the magnetic measurements characterize the magnetic state of the alloys over the whole range of compositions from NiFe to NiMn.

THE EXPERIMENT AND RESULTS

Bars of the alloys were melted in a high frequency furnace in an inert gas atmosphere. Carbonyl iron and electrolytic nickel and manganese were used as the starting materials. 21 alloys of constant nickel content (50 at.%) were prepared by gradual replacement of iron by manganese, starting from the binary alloy NiFe with zero manganese content and finishing with the binary alloy NiMn, in which the iron is completely replaced by manganese. The alloys were homogenized by annealing, forged, and then subjected to a temperature of 950°C for 30 minutes and rapidly quenched in water. Such a cycle of treatment, together with the attainment of grain dimensions of the order of 100 μ, ought to have

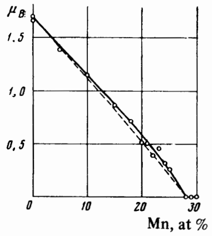

FIG. 1. Dependence on Mn concentration of the mean magnetic moment per atom in units of μ_B for Ni-Fe-Mn ternary alloys. The points and continuous line are experimental; the dotted line is calculated.

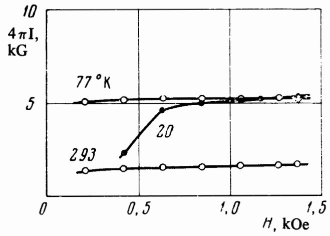

FIG. 2. Magnetization curves for the alloy with 20 at. % Mn at liquid hydrogen, liquid nitrogen and room temperatures.

ensured a disordered state in the samples. Metallographic analysis demonstrated that for all compositions the alloys were single-phase.

The concentration dependence of the saturation magnetization and of the magnetic susceptibility was measured on a ballistic apparatus by a commutation method at liquid hydrogen, liquid nitrogen and room temperatures in a solenoid producing a field of up to 1500 Oe. The magnetization of samples with 26 and 27 at.% Mn was measured in an oil-cooled solenoid in fields of up to 3000 Oe. The temperature dependence of the magnetic susceptibility was measured with a magnetic balance in the interval from liquid nitrogen temperature to room temperature in fields of up to 15 kOe.

In Fig. 1 (the continuous curve and points) is shown the dependence on the manganese content in the alloy of the mean magnetic moment per atom of the alloy, calculated from the saturation magnetization reduced to 0°K. Replacement of iron by manganese lowers the magnitude of the mean magnetic moment per atom, which decreases almost linearly up to 20 at.% Mn and then, going over to a steeper dependence, goes to zero at 28 at.% Mn.

The magnetization curves for the alloy containing 20 at.% Mn at liquid hydrogen, liquid nitrogen and room temperatures are shown in Fig. 2. It is clear that the magnetization is practically the same at the temperatures of liquid hydrogen and liquid nitrogen. The alloys are easily magnetized and saturation at liquid nitrogen and room temperatures is reached in fields of 500 Oe. The magnetization curves for all compositions up to 25 at.% Mn have the same character. Alloys containing 26 and 27 at.% Mn have, in contrast to all the others, a strong field-dependence for the magnetization and we did not succeed in bringing them to saturation in the fields of 3000 Oe used. Therefore, in Fig. 1 the values of the mean magnetic moment per atom corresponding to these two concentrations are not shown. But decrease of the magnitude of the magnetization with increase of manganese content in the alloy appears absolutely clearly at the compositions 26 and 27 at.% Mn.

For alloys containing 30 at.% or more Mn, the magnetic susceptibility was measured. In the alloy containing 30 at.% Mn, the field-dependence was so strong that it was difficult to make sufficiently reliable measurements. For the alloy with 35 at.% Mn, the susceptibility depends weakly on the field and is independent of it for 40, 45 and 50 at.% Mn (we used fields of up to 15 kOe). The temperature dependence, plotted at a field of 10 kOe, of the susceptibility of alloys containing 35, 40, 45 and 50 at.% Mn is shown in Fig. 3. From the figure it is clear that, for the last three compositions, χ does not change with temperature in the temperature interval investigated. The considerable temperature dependence of the susceptibility of the alloy containing 35 at.% Mn is not described by a Curie-Weiss law and does not enable us to isolate the temperature-dependent component of the susceptibility.

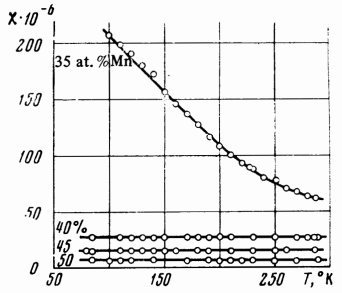

FIG. 3. Temperature-dependence of the magnetic susceptibility (in electromagnetic units per gram) of the alloys with 35, 40, 45 and 50 at. % Mn.

It is clear from Fig. 3 that the susceptibility of alloys, taken at fixed temperatures, is smaller the greater the Mn content in the alloy. The susceptibility of the alloy containing 50 at.% Mn is equal in magnitude to the value obtained in[2] for the ordered 1 : 1 composition NiMn. Evidently it is not possible to obtain the disordered state of this alloy by quenching from high temperatures.

DISCUSSION OF THE RESULTS

In alloys in which there are positive and negative exchange interactions, with atomic magnetic moments which are constant or vary only slightly with composition, the main role in the production of the mean magnetic moment is played, in the classical picture, by an orientation mechanism for the atomic magnetic moment vectors[9,10] or, in the quantum-mechanical picture, by a mechanism in which, owing to the competition between the two forms of exchange coupling, the z-components of the atomic spins compensate. It was remarked above that the character of the exchange coupling in the pairs Ni-Ni, Ni-Fe, Ni-Mn, Fe-Fe and Mn-Mn in ternary nickel-iron-manganese alloys is known by virtue of the analogy between these ternary alloys and the binary alloys Ni-Fe and Ni-Mn. The pairing of the neighboring atoms Fe-Mn occurring in the ternary alloys is characterized, in the opinion of the authors of[12], by negative exchange coupling. If the magnitudes of the atomic magnetic moments in the ternary alloys are assumed to be equal to the moments in the binary alloys Ni-Fe and Ni-Mn ($\mu_{Ni} = 0.6\ \mu_B$, $\mu_{Fe} = 2.8\ \mu_B$, and $\mu_{Mn} = 3.6\ \mu_B$), then the decrease in the mean magnetic moment per atom of the alloy, which we obtained experimentally for low concentrations of Mn in the triple alloys (see Fig. 1), can be explained only by a negative exchange interaction for the Fe-Mn pairs, stronger than the negative interaction for the Fe-Fe pairs.

Taking these observations into account in the approximations used in[9,10], we shall calculate the magnitude of the mean magnetic moment per atom for the unordered ternary nickel-iron-manganese alloys. We introduce the following notation: 1, 2 and 3 are the different kinds of atom, Ni, Fe and Mn respectively; c_1, c_2 and c_3 are the corresponding atomic concentrations of the components, and μ_1, μ_2 and μ_3 are the atomic magnetic moments. We suppose that the exchange integrals satisfy the conditions

$$I_{11} > 0, \quad I_{12} > 0, \quad I_{13} > 0, \tag{1}$$

$$I_{22} < 0, \quad I_{23} < 0, \quad I_{33} < 0, \tag{2}$$

$$|I_{22}| \leqslant |I_{23}| \approx |I_{33}|. \tag{3}$$

Thus, the spins in the atom pairs 1-1, 1-2 and 1-3 tend to be oriented parallel to each other, but antiparallel in the pairs 2-2, 2-3 and 3-3. As a result of this, the contribution of each kind of atom to the resultant magnetization of the alloy is diminished.

To calculate the mean magnetic moment per atom of the alloy it is necessary to determine the average effective number of nearest neighbors for all atoms with negative pair exchange interaction. Neglecting, in accordance with condition (3), the interaction in the 2-2 pairs, we determine $n_{3\mathrm{eff}}$, the average effective number of atoms 3 nearest to atoms 2 and 3. As is shown in[9-11], in calculating $n_{3\mathrm{eff}}$ one must take into account only those statistical fluctuations in the surroundings for which the number of nearest neighbors of type 3 is greater than or equal to some number x. Thus $n_{3\mathrm{eff}}$ denotes physically that account is taken only of those fluctuations in the surroundings in which the exchange interactions are sufficient to induce compensation of the z-component of the spin[11]. For a rough estimate of the nature of the mean magnetic moment per atom in nickel-iron-manganese ternary alloys, we assume that $I_{23} = I_{33}$. Hence it follows that the z-projections of the spins of atoms 2 and 3 are compensated when there are $n_3 \geq x$ atoms of type 3 around either of them.

Arguments and discussion elucidating the derivation of the formula for the mean magnetic moment per atom are expounded in detail in[9,10] and so, avoiding repetition, we write the expression for $\bar{\mu}$ for a ternary alloy:

$$\bar{\mu} = c_1(1 - n_{1\,\mathrm{eff}}\, n_{3\,\mathrm{eff}}\, \lambda_1\lambda_2)\mu_1 + (1 - n_{3\,\mathrm{eff}}\, \lambda_2)(c_2\mu_2 + c_3\mu_3), \tag{4}$$

where λ_1 and λ_2 are constant coefficients and $n_{1\mathrm{eff}}$ is determined for the condition $n_{1\mathrm{eff}} + n_{3\mathrm{eff}} = z$, where z is the first coordination number.

In a completely unordered three-component alloy any lattice site is occupied by an atom 1, 2 or 3 with probability c_1, c_2, c_3 respectively. The probability that any lattice site is surrounded by n_1 of atom 1, n_2 of atom 2 and n_3 of atom 3 satisfies the polynomial distribution

$$P_z(n_1, n_2, n_3) = \frac{z!}{n_1!n_2!n_3!} c_1^{n_1} c_2^{n_2} c_3^{n_3}. \tag{5}$$

It is clear that

$$n_1 + n_2 + n_3 = z. \tag{6}$$

To calculate $n_{3\mathrm{eff}}$ we must multiply (5) by n_3 and sum over all possible combinations of values of n_1, n_2 and n_3 for $n_3 \geq x$ and take account of (6), since only two of the three values n_1, n_2 and n_3 can vary independently. Thus,

$$n_{3\,\mathrm{eff}} = \sum_{n_2, n_3 \geqslant x} \frac{z!}{n_1!n_2!n_3!} c_1^{n_1} c_2^{n_2} c_3^{n_3} n_3. \tag{7}$$

The constant coefficients λ_1 and λ_2 are determined, as was assumed in[9,10], from the condition that the coefficients of μ_1 and $c_2\mu_2 + c_3\mu_3$ (the bracketed expressions in formula (4)) simultaneously and independently go to zero:

$$1 - n^0_{1\,\mathrm{eff}}\, n^0_{3\,\mathrm{eff}}\, \lambda_1\lambda_2 = 0, \quad 1 - n^0_{3\,\mathrm{eff}}\, \lambda_2 = 0, \tag{8}$$

where $n^0_{1\mathrm{eff}}$ and $n^0_{3\mathrm{eff}}$ are the values of $n_{1\mathrm{eff}}$ and $n_{3\mathrm{eff}}$ for $c_3 = c_3^0$; and c_3^0 is the experimentally-determined concentration of component 3 for which $\bar{\mu} = 0$. In the case of the ternary nickel-iron-manganese investigated by us, $c_3^0 = 0.28$.

The value of x is chosen starting from the following considerations. As was shown by study of the binary Ni-Mn alloys[9], the smallest number of Mn atoms, near to a manganese atom, required to induce compensation of the z-component of the spin is equal to three, i.e., x = 3. Since we assume that the exchange interaction is the same for the Mn-Mn and Fe-Mn pairs it would follow that we should also take this value for the ternary system. However, it is necessary to take into account that in these alloys (in the range of concentrations for which there is still spontaneous magnetization) there is always a large number of Fe-Fe pairs with weak negative exchange interaction. Therefore, we can assume that compensation of the spins of the Mn and Fe atoms will occur at a lower critical amount of Mn atoms. On this basis we used the value x = 1 in the calculations. This corresponds physically to the assumption that the occurrence near a Mn or Fe atom of only one nearest Mn atom is sufficient to compensate the z-component of the spin of the corresponding atom. This simplifies the expression for $n_{3\mathrm{eff}}$, which is simply equal to the average number of atoms 3 around each 2 or 3 atom, $n_{3\mathrm{eff}} = zc_3$.

Using the fact that $c_1 = \text{const.} = 0.5$, the values of $\bar{\mu}$ are calculated by the formula, obtained from (4):

$$\bar{\mu} = 0{,}5[1 - z^2 c_3(1 - c_3)\lambda_1\lambda_2]\mu_1 + (1 - zc_3\lambda_2)(c_2\mu_2 + c_3\mu_3), \tag{9}$$

and are shown in Fig. 1 by the dotted line. The values taken for the atomic magnetic moments are the same as those for the binary alloys Ni-Fe and Ni-Mn. As is clear from the figure, the calculated curve satisfactorily describes the experimental dependence on the composition of the mean magnetic moment per atom of the alloy.

This fact allows us to draw the following conclusions.

1) In the ternary nickel-iron-manganese alloys the mean magnetic moment is produced by the same mechanism as in the binary alloys Ni-Fe, Ni-Mn, Pt-Mn and Pd-Fe[6,8,13].

2) The exchange interactions for the pairs Fe-Mn and Mn-Mn clearly have the same sign and are close in magnitude. Evidently, it is possible that on change of the Mn content in ternary alloys there is some range of concentrations for which the positive and negative exchange interactions (which in limiting cases lead to ferro- or antiferromagnetic structure) influence the

formation of the magnetic structure to approximately the same extent. The magnetic state in the region of such compositions must be unstable and sensitive to the imposition of external magnetic fields. The existence of a strong field dependence of the magnetic properties in ternary nickel-iron-manganese alloys on both sides of the concentration 28 at.% Mn, the point at which the mean magnetic moment disappears, is in accordance with such ideas. Increase in the alloy of the content of Mn, the strongly antiferromagnetic component, leads to increase of the total negative exchange interaction, which ultimately produces long-range antiferromagnetic ordering, as is observed for the 1 : 1 alloy NiMn.

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