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# Study of Anomalous Microregions in Ferromagnetic Substances by Means of $\gamma$-Resonance Spectroscopy

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We have observed local inhomogeneities in ferromagnetic solid solutions that lead to the appearance of supermagnetic clusters of the $Fe_3Al$ type with magnetic moments $\sim 150\mu_B$, and containing about $\sim$ 100 Fe atoms. Two other possible positions of the Fe atoms differing with respect to magnetic moments may exist in a solid solution. It is shown that the distribution of the Fe atoms with respect to the three possible positions depends on the alloy composition and degree of atomic order.

THE existence of local inhomogeneities in magnetically-ordered substances gives rise to magnetic clusters, which are regions separated from the main matrix by nonmagnetic atoms[1-4]. The study of such inhomogeneities contributes to the understanding of the anomalies in the physical, particularly magnetic, properties of many substances. We have investigated Fe-Al clusters observed in Fe-Ni-Co-Al solid solutions[5,6]. Such alloys are of interest because it is possible to vary the concentration of the magnetic atoms by means of the nonmagnetic diluent atoms (Al) and consequently vary the magnitude and character of the exchange interactions in the system.

The investigated samples were prepared by melting the components in an arc furnace in an atmosphere of purified argon. The purity of the initial materials was not worse than 99.9%. An x-ray analysis has shown that the samples are single-phase and have a BCC crystal lattice with order of type $B_2$ (FeAl). The sample compositions are listed in Table I. All alloys were ferromagnetic. The smallest saturation magnetization at 300°K (35 G) was possessed by sample 1. The Mossbauer spectra were obtained with a $\gamma$-resonance spectrometer at constant acceleration. The radiation detectors were a photomultiplier (FEU-37) with an NaI(Tl) crystal 0.1 mm thick and a proportional counter filled with Kr. In all the measurements, the $Co^{57}$(Cr) source was at constant temperatures. The absorbers were made of powders obtained in agate mortars. The absorber temperature ranged from 4.2 to 300°K. External magnetic fields $H_0 = 20-25$ kOe were used. The magnetic field was parallel to the $\gamma$-quantum beam at 3.2°K (permanent magnet).

The Curie temperature of sample 1 is ~500°K, but the $Fe^{57}$ absorption spectra of this sample shows only single lines with width $2\Gamma = 0.55$ mm/sec. The magnetic hyperfine structure (hfs) appears only below 15°K (Fig. 1). Thus, the temperature dependence of the effective magnetic moments of the Fe atoms ($\mu_{Fe}$), determined from the $\gamma$-resonance spectra, differs strongly from the corresponding dependence of the average macroscopic moment of the alloy. The spectrum of sample 1 at 4.2°K in a longitudinal magnetic field is shown in Fig. 2. The measurement in the magnetic field enables us to interpret the upper spectrum of Fig. 1 as consisting of two systems of hfs lines and a central single line. The positions of the outer lines of both hfs systems and of the single line split in the external field are shown by vertical bars in Fig. 2. The effective magnetic fields $H_{eff\,1,2}$ of the positions of the centers of gravity of the spectral components (relative to Armco iron) are given in Table II.

**Table I**

| Sample No. | Composition (at.%)* | | | |
|---|---|---|---|---|
| | Fe | Al | Co | Ni |
| 1 | 15 | 42 | 24 | 19 |
| 2 | 15 | 37 | 24 | 24 |
| 3 | 15 | 27 | 39 | 19 |

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*We used Fe with natural $Fe^{57}$ content.

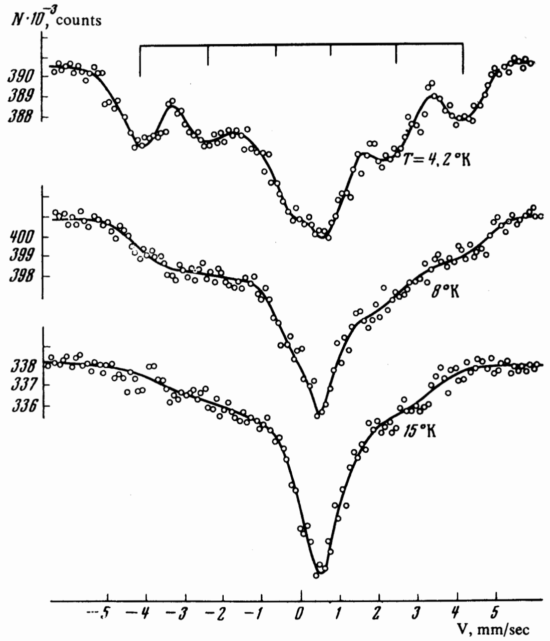

FIG. 1. Mossbauer spectra of sample 1 at different temperature. $Co^{57}$(Cr) source at 300°K. The vertical bars show the positions of the lines of the proposed magnetic hyperfine structure with field $H_{eff\,1}$.

Thus, alloy 1 contains at 4.2°K three types of Fe atoms with different 3d-shell structures; this causes the difference in the magnetic moments. The observed decrease of $H_{eff}$ for both hfs systems, when the external field is turned on indicates, as is well known, an ordering of the ferromagnetic type for the correspond-

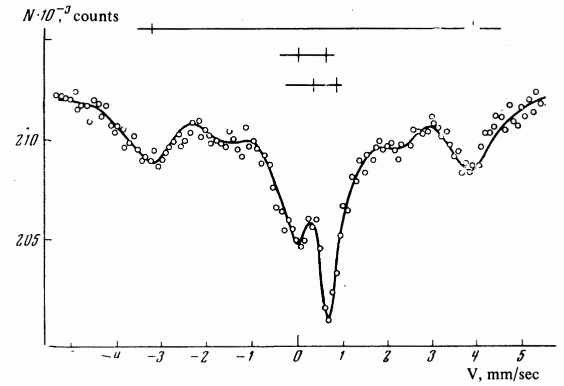

FIG. 2. Mossbauer spectrum of sample 1 at T = 4.2°K in a longitudinal magnetic field $H_0$ = 25 kOe. $Co^{57}$ source at 300°K. The positions of the outermost lines of the hfs systems with fields $H_{eff\,1}$ and $H_{eff\,2}$, and of the central line split in the external field, are shown.

Table II

| Sample No. | $H_0$, kOe | T, °K | $H_{eff}$ ± 10, kOe | δ ± 0.1, mm/sec |
|---|---|---|---|---|
| 1 | — | 4.2 | 250 (1)<br>50 (2)<br>— (3) | 0.4<br>0.4<br>0.6 |
| 1 | 20—25 | 4,2 | 230 (1)<br>20 (2)<br>20 (3) | 0.4<br>0.4<br>0.6 |
| 2 | 21 | 300 | 180 * | 0.2 |
| 2 | — | 300 | — | 0.2 |
| 3 | — | 300 | 320 (1)<br>160 (2)<br>260 (3) | 0.1<br>0.1<br>0.1 |

*The value of $H_{eff}$ for sample 2 in the magnetic field was estimated from the line half-width.

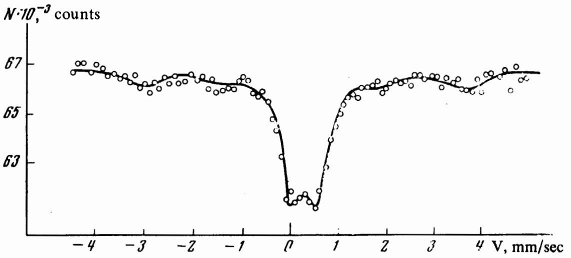

FIG. 3. Mossbauer spectrum of sample 1 after annealing (700°C, 4 hours). Sample at T = 4.2°K in a longitudinal magnetic field $H_0$ = 25 kOe. $Co^{57}$ (Cr) source at 300°K.

ing Fe atoms. The character of the interaction of the Fe atoms responsible for the single line in the spectrum can be determined by one of two mechanisms. It is possible that this line is connected with Fe atoms having no localized magnetic moment. On the other hand, antiferromagnetic ordering of the Fe atoms can also cause the appearance of such a line. Arrot and Sata[7] found antiferromagnetic ordering at low temperatures in the binary Fe-Al alloys. The more probable of these two possibilities is the first. Indeed, Frankel et al.[8] measured the hfs parameters of $Fe^{57}$ atoms introduced into ordered alloys of equi-atomic composition FeAl, NiAl, and CoAl at helium temperatures, in external fields up to 80 kOe, and have shown that the electron structure of the Fe atoms in FeAl and NiAl is such that there are no localized magnetic moments. We propose that the single line on Fig. 1 is due to Fe atoms situated in an ordered solid solution and having $\mu_{Fe} = 0$. Obviously, the nearest surroundings of such atoms should consist of Al. The interaction of the Fe atoms with the neighboring Al atoms should influence most strongly the value of $\mu_{Fe}$, and consequently $H_{eff}$, in comparison with the Fe-Co and Fe-Ni interactions[9]. The hfs system with the larger field $H_{eff\,1}$ can be attributed to the existence of an ordered phase $Fe_3Al$ in the binary Fe-Al system. The unusual temperature dependence of the field $H_{eff\,1}$, which is close to zero already at 15°K whereas the Curie temperature $T_c$ of the alloy is 500°K, forces us to assume the presence of superparamagnetic properties in regions of the $Fe_3Al$ type located in the solid-solution matrix. The total magnetic moment of such clusters changes direction spontaneously as a result of thermal fluctuations. The magnetic hfs disappears when the characteristic time $\tau$ of the magnetic-moment relaxation is such that $\tau \ll \tau_L$, where $\tau_L$ is the time of the Larmor precession of the spin of the nucleus $Fe^{57m}$ in the field $H_{eff}$. In a 250-kOe field we have $\tau_L \sim 10^{-8}$ sec and consequently $\tau \ll 10^{-8}$ sec at T > 15°K and $\tau > 10^{-8}$ sec at 4.2°K. The increase of $\tau$ in an external magnetic field at 4.2°K can no longer be revealed by $\gamma$-resonance spectroscopy. As to the field $H_{eff\,2}$, we can assume on the basis of the results of Frankel et al.[8] on CoAl that the field $H_{eff\,2}$ corresponds to those Fe atoms in the solid solutions, some of whose nearest Al neighbors are replaced by Co.

Using the data on the concentration dependence of $H_{eff}$ (T = 4.2°K) for binary Fe-Al alloys[3,9,10], we can estimate the Al content in the $Fe_3Al$-type regions in the matrix solid solution. According to these estimates, the Al content is 33 and 48%, respectively. The possible appearance of local inhomogeneities in the investigated alloys is confirmed by the data of[11] on diffuse scattering of x-rays in binary Fe-Al alloys (30—40 at.%) and in Fe-Ni-Al alloys[12].

The distribution of the Fe atoms over the three possible positions (with different surroundings) depends strongly on the degree of atomic order in the alloy. In sample 1, after annealing (700°C, 4 hours) the intensity of the type $B_2$ superstructure lines on the x-ray pattern increases. The Mossbauer spectra of the annealed sample at 300 and 85°K do not differ from the spectra obtained prior to annealing. Significant changes in the spectrum of the annealed sample are observed at 4.2°K. Figure 3 shows the spectrum of this sample at 4.2°K in a magnetic field. The distance between the peaks on Fig. 3 corresponds to the applied field. In the case of binary Fe-Al alloys with ordering of the Fe-Al type, annealing at 700°C leads to a disruption of the $Fe_3Al$-type order and to appearance of an order of the FeAl type. The regions of the $Fe_3Al$ type are apparently destroyed in the investigated alloy. After annealing, most Fe atoms have no localized moments and are in regions of the FeAl type. The weak hfs lines on Fig. 3 correspond to the still remaining regions of the $Fe_3Al$ type.

The spectrum of sample 2 is shown in Fig. 4. The spectrum was obtained at 300°K without a magnetic field (upper part) and in a transverse field (lower part). We see that application of the external field stabilizes

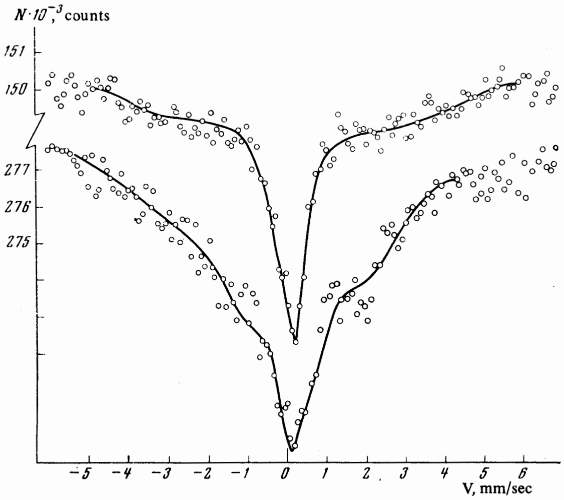

FIG. 4. Mossbauer spectra of sample 2 at T = 300°K. Upper curve–$H_0 = 0$, lower curve–$H_0 = 21$ kOe (transverse field). $Co^{57}(Cr)$ source at 300°K.

the magnetic moments of most Fe atoms. It follows therefore that in this alloy, too, there exist superparamagnetic clusters whose magnetic moments are stabilized by the external field. We can roughly estimate the dimensions of the clusters and their magnetic moments, assuming that their composition is close to $Fe_3Al$. We then obtain $\mu H_0 \sim kT$, where $H_0 = 20$ kOe, k is Boltzmann's constant, and T = 300°K. The magnetic moment of the cluster is $\mu = 150\ \mu_B$. The cluster contains ~100 Fe atoms, corresponding to a linear dimension ~10 Å. The magnetic moment of the cluster can be stabilized also by another method, by lowering the sample temperature. In the case of alloy 2, such a stabilization occurs already at 85°K. The spectrum of sample 2 at this temperature comprises a system of hfs lines. An increase of the Al concentration in the alloy (sample 1) decreases the magnetic moments of the Fe atoms making up the clusters. The decrease of the magnetic moments $\mu_{Fe}$ decreases also the temperature $T_{st}$ at which the total magnetic moment of the cluster becomes stabilized. For sample 1, this temperature is thus shifted into the region of helium temperatures.

The ideas advanced above allow us to proceed to the analysis of the spectrum of sample 3 (Fig. 5). In this spectrum, obtained at 300°K, we can distinguish two systems of hfs lines, corresponding to zero and four Al atoms among the nearest neighbors of the Fe atoms, i.e., regions of the $Fe_3Al$ type. Located between these hfs systems is a system of lines corresponding to three Al atoms in the first coordination sphere, corresponding to the alloy matrix. We note that no regions of the type $(Fe, Ni, Co)_3Al$ are apparently produced in the investigated alloys. Indeed, as seen from Fig. 1, only about 10% of the Fe atoms are contained in the solid-solution matrix that ensures the ferromagnetism of the alloy at 300°K. If a similar ratio is retained for the Co and Ni atoms, the resultant values of the average magnetic moment per magnetic atom in the alloy (~1 $\mu_B$) is anomalously large in comparison with the Mossbauer data (~0.2 $\mu_B$). The estimate was obtained under the assumption that the moments of Co and Ni in the solution matrix do not differ greatly from the moment of Fe, the latter being extrapolated to 300°K from the critical temperature 500°K (the Curie temperature of alloy 1) with the aid of the Brillouin function.

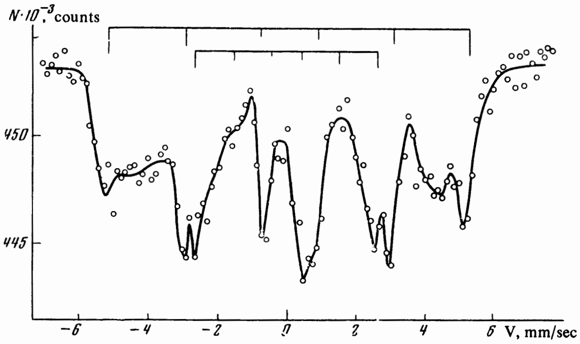

FIG. 5. Mossbauer spectrum of sample 3 at 300°K. $Co^{57}(Cr)$ source at 300°K. Two hfs systems, corresponding to zero and four Al atoms among the nearest neightbors of Fe, are shown.

Thus, Mossbauer-spectroscopy studies of Fe-Co-Ni-Al alloys have established the following. The Fe atoms occupy three characteristic positions in the investigated ferromagnetic solid solutions, which have a type-$B_2$ order (FeAl) and are single-phase according to the x-ray data. Some of the Fe and Al atoms form superparamagnetic clusters of the $Fe_3Al$ type. The estimated dimension of these clusters is ~10 Å. In the main matrix of the alloy, there exist two other positions of the Fe atoms, with different magnetic moment. This difference is connected with the nearest surrounding of the Fe atoms. It is assumed that in one case, owing to the strong interaction of the Fe and Co atoms, the number of Co atoms among the nearest neighbors of Fe increases. In the other case, the surrounding of the Fe corresponds to the ordered alloy FeAl. The distribution of the Fe atoms among the three possible positions depends on the composition of the alloy and on the degree of the atomic order. At $T < T_c$, the Fe atoms in the investigated alloys contribute to the summary magnetic moment only below a certain temperature $T_{st}$ at which the magnetic moments of the clusters begin to stabilize. $T_{st}$ decreases with increasing Al content.

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