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Distribution of local magnetic moments in Mn over inequivalent lattice sites in quasibinary (Fe₁₋ₓMnₓ)₃ Al alloys

Distribution of local magnetic moments in Mn over inequivalent lattice sites in quasibinary $(Fe_{1-x}Mn_x)_3$ Al alloys

M. Wolf[1], S. Mager[1], P. N. Stetsenko, V. V. Surikov, and S. I. Kasatkin

Moscow State University
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Nuclear spin echo and magnetic diffuse scattering of neutrons by Mn^{55} nuclei in quasibinary $(Fe_{1-x}Mn_x)_3$ Al alloys are investigated. Three regions of resonant absorption corresponding to three different positions of the Mn ions in the Fe_3Al lattice are observed. The moments of Mn at various sites are determined from the magnetic moments obtained by neutron diffraction and averaged over the lattice. The NMR and neutron-diffraction data indicate that Mn atoms with an antiferromagnetic orientation of the local magnetic moments appear when the Mn concentration in the alloy increases.

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Fe–Mn–Al alloys, just as Fe–Cr–Al alloys, have high electric resistivity ($\rho = 1.5$–$2\ \Omega$-mm²/m) at relatively high magnetization. The anomalies observed in the temperature dependence of the resistivity, particularly the presence of smeared out minima of ρ in wide temperature ranges, [1] can be due to the specific character of the electronic structure of these alloys and to singularities of the behavior of the local magnetic moments in them. The most important circumstance is that in these systems exchange interactions of both the ferro- and anti-ferromagnetic type take place, and leads to appreciable changes in the local characteristics when the atomic environment is varied.

A particularly acute problem is the determination of the local magnetic moments of the manganese and iron atoms ($\mu(Mn)$ and $\mu(Fe)$) in these alloys. However, neutron-diffraction methods yield only local magnetic moments of all the alloy components averaged over the lattice, and do not make it possible to investigate the distribution of the moments over the non-equivalent lattice sites and to ascertain the role of the atomic environment. At the same time, methods of investigating hyperfine interactions, and especially methods of measuring the nuclear spin echo, have exceptionally high resolving power and measurement accuracy, but it is quite difficult or impossible to determine the absolute values of the local magnetic moments. Naturally, optimal results can be obtained by combining these methods.

We have investigated the magnetic diffuse scattering of neutrons and nuclear spin echo on the nuclei Mn^{55} in the quasi-binary alloys $(Fe_{1-x}Mn_x)_3Al$. The neutron-diffraction investigations were carried out at the Central Institute of the Solid State Physics and Metallurgy and the Central Institute for Nuclear Research of the Academy of Sciences of the German Democratic Republic in Dresden, while the nuclear spin echo was investigated at the Moscow State University. The samples for the measurements were smelted in an induction furnace with strong cooling. The quenched ingots were reduced in ball grinders to a powder with particle dimensions not larger than 50 μm. The concentrations of the manganese and the aluminum in the investigated samples are listed in Table I.

The nuclear spin echo on the Mn^{55} nuclei was measured with a spectrometer operating in a wide frequency band, using pulses of 1 μsec duration and with 15 μsec

TABLE I.

Sample No.	C(Mn), at.%	C(Al), at.%	$\bar{\mu}$, μ_B	$\bar{\mu}$ (Fe), μ_B	$\bar{\mu}$(Mn), μ_B
1	3.4	24.4	1.37	2.0	2.0
2	7.0	24.9	1.18	1.7	1.7
3	9.4	24.9	1.06	1.7	0.7
4	13.9	25.5	0.89	1.5	0.7
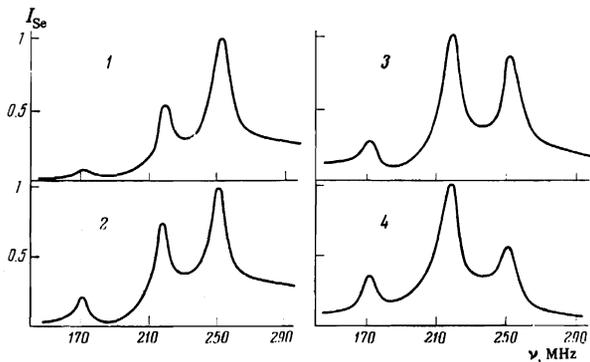
FIG. 1. Nuclear spin-echo spectra of the system $(Fe_{1-x}Mn_x)_3Al$ at $T = 4.2°K$ (I_{Se}—intensity of spin echo, normalized scale; ν—resonance frequency, designated f in the text).

pauses between them. The measurements were performed mainly at $4.2°K$, although some measurements were made also at 1.5 and $80°K$. Figure 1 shows spectra of the nuclear spin echo on Mn^{55} in the investigated alloys. A characteristic feature of these spectra is the presence in them of three regions of resonant absorption at the frequencies $f_1 = (172 \pm 2)$ MHz, $f_2 = (219 \pm 2)$ MHz, $f_3 = (252 \pm 2)$ MHz. These resonances correspond to three values of the effective magnetic field at the Mn^{55}: $H_1 = -164 \pm 2$ kG, $H_2 = -208 \pm 2$ kG, and $H_3 = -240 \pm 2$ kG. The sign of the effective field was not determined in our measurements, but the data for the Fe—Mn binary alloys[2] and the general laws governing the behavior of the effective fields[3] allow us to regard the fields at the Mn^{55} nuclei in the alloys $(Fe_{1-x}Mn_x)_3Al$ to be negative. The frequency of the resonance lines is not shifted with changing concentration of the alloys, but an appreciable change is noticed here in the relative intensity of the resonance lines.

It should be noted that the very broad frequency band in which resonance on Mn^{55} is observed (~ 100 MHz) indicates that the change of H_i of these alloys cannot be due to the influence of the atomic environment alone, and points to appreciable changes in $\mu(Mn)$ over the alloy lattice sites. When the resonance lines of the spectrum are indexed, it is natural to relate them with three types of sites in the Fe_3Al crystal. It is known that in the lattice of the ordered binary alloy Fe_3Al the iron atoms occupy vertices of cubes (Fe_I) and centers of small cubes (Fe_{II}), while the aluminum atoms occupy centers of the large cube centers (Al). According to structure-investigation data,[4] Fe—Mn—Al alloys containing not more than 20 at.% manganese are solid solutions that become ordered in the Fe_3Al pattern. The manganese atoms occupy predominantly the sites Fe_I and Fe_{II}, and their number in Al sites is negligible. Consequently, the peak with the minimum intensity ($f_1 = 172$ MHz) can be compared with the manganese atoms occupying the Al sites. Next, the number of Fe_{II} sites is double the number of Fe_I sites, and consequently, the peak with the maximum intensity ($f_3 = 252$ MHz) must be set in correspondence with the Fe_{II} sites. Thus, the central line ($f_2 = 219$ MHz) corresponds to manganese atoms situated in the Fe_I sites. A decrease in the relative intensity of the $f_3 = 252$ MHz line for samples 3 and

4 containing the maximum amount of manganese is due, as will be shown below, to the fact that the orientation of a certain part of $\mu(Mn)$ reverses orientation and becomes antiparallel (relative to the direction of the average moment). The integrated intensity of the resonance lines was used to calculate the parameters P_{ij} that determine the relative content of the manganese atoms in the i-th sites of the j-th sample.

The table lists the values of the local moments of manganese and iron, averaged over the volume, and determined by a neutron-diffraction method for the same alloys in which the spin-echo spectra were measured.[5] The measurements of the magnetic diffuse scattering of the neutrons were made in an external magnetic field of 4.5 kOe. The calculated effective cross sections were corrected to take into account the multiple scattering, the thermal diffuse scattering, and the absorption. The determination of $\mu(Fe)$ and $\mu(Mn)$ was carried out under the assumption that $\mu(Al) = 0$, and that the delocalized magnetic moment of the alloy is due mainly to the presence of the iron and amounts to -0.12 μ_B per atom. The table lists also the alloy magnetizations measured by a ballistic method. These data, jointly with the experimental results of measurements of the spin echo, have made it possible to construct the system of equations

$$\sum_i P_{ij}\mu_i = \bar{\mu}_j, \quad a\mu_i + b\bar{\mu}_j = H_i, \tag{1}$$

where the subscripts $i = 1, 2, 3$ correspond to the crystallographic positions of the lattice sites, while $j = 1, 2, 3, 4$ corresponds to the given sample (see the table). The solution of the system (1) has made it possible to determine the local magnetic moments of the manganese for the three types of sites: $\mu(Mn) = 0.4$ μ_B, 1.6 μ_B, and 2.4 μ_B for Al, Fe_I, and Fe_{II}, respectively. These values of $\mu^i(Mn)$ are determined by the configuration of the environment typical of the given type of site, and do not change with changing concentration of the alloy. The decrease of the average moment of the manganese takes place as a result of the change of its concentration in various sites and as a result of the change in the direction of the moments for part of the manganese atoms situated at the Fe_{II} sites. The variation of $\mu^i(Mn)$ as a function of the type of site is determined to a considerable degree by the presence of iron atoms in the nearest coordination spheres. As shown earlier,[6] in Fe—Mn—Ni alloys the increase of the number of iron atoms in the nearest environment of the manganese leads to an appreciable decrease of $\mu(Mn)$. The same regularity appears also in Fe—Mn—Al alloys. For the Fe_{II} sites in the first coordination sphere, there are 4 aluminum atoms and 4 iron atoms; for the Fe_I sites the first coordination sphere is completely filled with iron atoms, while the second sphere is filled with aluminum atoms. For the Al sites, the first and second coordination spheres are completely filled with iron atoms.

The physical mechanism of variation of $\mu^i(Mn)$ may be connected with the change of the interaction energy, for example, the energy of the intra-atomic Coulomb interaction, and also the change of the local density of

the electronic states with changing number of neighboring iron atoms. In addition, $\mu^i(Mn)$ can be greatly influenced by the delocalized spin density, the spatial distribution of which has a complicated character and depends to a considerable degree on the type and the distribution of the neighboring atoms.

The solution of the system (1) has made it possible to determine the coefficients of the hyperfine interaction in the relation

$$H^i(Mn) = a\mu^i(Mn) + b\bar\mu,$$

which turn out to be $a = -40$ kG/μ_B and $b = -100$ kG/μ_B. The values of these coefficients point to an appreciable degree of delocalization of the spin density in the alloys $(Fe_{1-x}Mn_x)_3Al$.

For samples 3 and 4 with maximum manganese contents, we determined also the relative numbers of manganese atoms with antiferromagnetic orientation $\mu(Mn)$. It turned out that for sample 3 about 50% of the manganese atoms situated at the Fe_{II} sites have antiferromag-netic orientation. For sample 4, this value is 60%. This conclusion is confirmed also by neutron-diffraction data, which have established the presence of manganese-enriched segregations in samples 3 and 4. The probability of flipping of $\mu(Mn)$ in such segregations, by virtue of the negative exchange interaction between the neighboring manganese atoms, can be quite high.

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Contribution to spin-spin cross relaxation theory

V. A. Atsarkin, V. G. Kustarev, and M. I. Rodak

Institute of Radio and Engineering, USSR Academy of Sciences

Evolution of the spin system of a solid paramagnet after the sudden introduction of frequency detuning Δ between the subsystems involved in cross relaxation (CR) is considered. The calculation is carried out by the density-matrix technique using projection operators and is applied to the general case of nonequidistant EPR and NMR spectra. It is shown that after a time of the order of ω_d^{-1} (ω_d is the local field frequency) the energy of the nonsecular part of the spin-spin interactions, which is responsible for the CR, is mixed with a part of the Zeeman energy, thus forming a quasiequilibrium "difference" pool. At $|\Delta| \gg \omega_d$ the process resembles damped oscillations and can be related via a Fourier transformation to the function between the CR probability and Δ. An experiment is proposed by which the predicted effects may be observed and employed for investigation of spin-spin interaction in solids.

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1. INTRODUCTION

The study of the processes of cross relaxation (CR) in parametric spin systems has already been the subject of hundreds of theoretical and experimental studies (see, e.g., [1-5]), but many important aspects of this phenomenon still remain unclear and continue to attract attention of researchers. One such unsolved problem is connected with the behavior of that of the "nonsecular" terms of the Hamiltonian of the dipole-dipole (DD) interactions,[1] which induces mutual spin flips I and S with close resonant frequencies ω_I and ω_S. For pure spin magnetism, it takes the form[1]

$$\hat{\mathcal{H}}_{CR} = \sum b_{ij}(\hat{I}_i^+\hat{S}_j^- + \hat{I}_i^-\hat{S}_j^+).$$

Although with respect to its specific heat this term can be comparable with the secular part $\hat{\mathcal{H}}_d'$ of the DD interactions, its contribution to the total energy balance is not taken into account in the spin-temperature theory of CR.[2,3] This contradiction manifests itself clearly on going to the "resonant CR," corresponding to the exact agreement of the frequencies ω_I and ω_S, while CR with large detuning $\Delta = \omega_I - \omega_S \gg \omega_d$, where ω_d is the average frequency of the dipole-dipole pool (DDP). Whereas in the former case the term $\hat{\mathcal{H}}_{CR}$ becomes secular and is included in the DDP, in the latter case its specific heat is neglected, so that the increase of Δ seems to be connected with the "vanishing" of the energy stored in $\hat{\mathcal{H}}_{CR}$. This seems particularly paradoxical if the DDP is strongly cooled beforehand by any one of the known methods.

In the recent literature two trends are noted in the solution of this problem, which turned out to be closely