Anomalies in the Mössbauer spectra of Sn^{119} nuclei in the region of the magnetic phase transition in yttrium iron garnets

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An investigation of the Mössbauer spectra of the Fe^{57} and Sn^{119} nuclei in the garnets $Y_{3-x}Ca_xFe_{5-x}Sn_xO_{12}$ ($x = 0.70$ and 0.90) near the Néel point T_N shows that there is a certain temperature range above T_N in which the tin nuclei Sn^{119} still feel the "traces" of magnetic order in the sample, whereas the iron nuclei Fe^{57} are no longer sensitive to it. This anomaly is discussed on the basis of relaxation effects. A possible effect of the covalent bonding and the spin-orbit interaction on the slowing down of the relaxation processes at the tin is proposed.

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INTRODUCTION

Reports have recently appeared on the observation of anomalous behavior of the Mössbauer spectra of ferrimagnets, both pure and substituted by diamagnetic ions, near their magnetic-ordering temperature T_N[1-5]. These anomalies consist in the fact that, as T_N is approached from the low-temperature side, starting from a certain temperature T_p additional peaks, corresponding to the paramagnetic state of the iron ions, appear against the background of the Zeeman hyperfine splitting in the Mössbauer spectrum. Thus, in the region $T_p < T < T_N$ "mixed" Mössbauer spectra are observed, indicating the simultaneous existence of ferri- and paramagnetic regions in the crystal.

Several causes that could lead to such an effect have been discussed. One of the causes is a local inhomogeneity of the sample, which could entail a certain distribution of ordering temperatures T_N and could lead to a smeared-out transition. Another cause could be associated with the relaxation of the electron spins of the iron ions in a time comparable with the period $\tau_L \approx 10^{-8}$ sec of the Larmor precession of the nucleus. In this case, either relaxation of the spins of the individual ions, or collective superparamagnetic relaxation in which the magnetic moments of certain assemblies of iron ions (clusters) fluctuate, can be realized[2]. An analysis of the experimental data recently obtained for yttrium iron garnet substituted with scandium, with the use of external magnetic fields, has shown that the latter mechanism is the most likely cause[3].

In this paper we report the discovery of a completely new type of anomaly, opposite in a certain sense to those that have been observed previously: while investigating the Mössbauer spectra of the Fe^{57} and Sn^{119} nuclei in the garnets $Y_{3-x}Ca_xFe_{5-x}Sn_xO_{12}$ near T_N we have found that there exists a certain temperature range above T_N in which the tin nuclei Sn^{119} still feel, as it were, the traces of magnetic order, while the iron nuclei Fe^{57} are no longer sensitive to it.

EXPERIMENTAL RESULTS

A. The Samples

In our previous papers[6-8] studying the temperature dependence of the magnetic fields at the Fe^{57} and Sn^{119} nuclei in the ferrite-garnet system $Y_{3-x}Ca_xFe_{5-x}Sn_xO_{12}$ we drew attention to the unusual behavior of the spectra of the Sn^{119} nuclei near T_N. In order to study the character of these anomalies in more detail we have given special attention, above all, to the preparation of single-phase samples homogeneous in composition, to stabilizing the temperature and to the uniformity of the heating of the sample during the measurements.

By ceramic technology, single-phase samples of garnets with $x = 0.70$ and $x = 0.90$ were prepared; the original iron and tin oxides were enriched in the isotopes Fe^{57} and Sn^{119}. The parameters of the cubic unit cell were found to be equal to 12.4725 ± 0.0015 Å for $x = 0.70$ and 12.4910 ± 0.0015 Å for $x = 0.90$, which agree with the data of[9]. It was established earlier[9-11] that the tin ions are arranged on an octahedral sublattice of the garnets, and therefore the cation distribution is described by the formula $\{Y^{3+}_{3-x}Ca^{2+}_x\}[Fe^{3+}_{2-x}Sn^{4+}_x] \times (Fe^{3+}_3)O_{12}$. For precision measurements in the region of the Néel point the temperature of the sample was stabilized and measured by means of a special electronic block with accuracy better than ± 0.5 K. The sample was situated in a specially constructed oven[12], ensuring zero-gradient heating of the sample, within the error bars of the measurements.

B. Spectra of the Fe^{57} Nuclei

In the paramagnetic temperature range the Mössbauer spectra of the Fe^{57} nuclei are a superposition of two quadrupole doublets, corresponding to the octahedral and tetrahedral positions of the Fe^{3+} ions. On passing through the Néel point T_N the spectra broaden sharply, because of the fact that an effective magnetic field begins to act on the Fe^{57} nuclei. As the temperature is lowered further, a well-resolved magnetic hyperfine structure appears in the spectra. The total width of the spectrum is a convenient characteristic for studying the phenomena near T_N, where the magnetic hyperfine structure is not resolved in detail[13,14].

The temperature dependence of the total width Γ of the spectra of the garnets studied is shown in the figure. At high temperatures the values of the width are constant. As the temperature is lowered, a sharp increase in the width occurs at a certain point, indicating the onset of magnetic order in the sample. We shall regard this point, by definition, as the Néel temperature T_N of the garnet. The values of T_N found in this way are 373 ± 1 K for $x = 0.70$ and 298 ± 1 K for $x = 0.90$. These values agree well with the T_N obtained from magneti-

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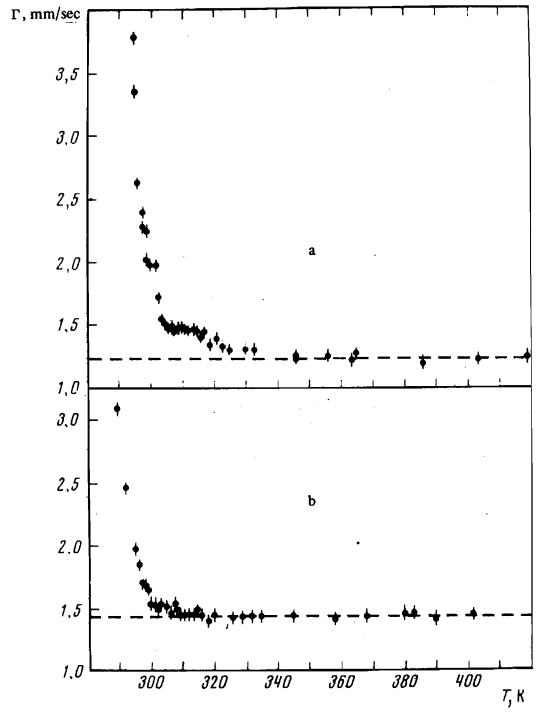

Dependence of the total linewidth Γ of the Mössbauer spectra for Sn^{119} (a) and for Fe^{57} (b) on the temperature T in the region of the Néel point in the garnet $Y_{2.1}Ca_{0.9}Fe_{4.1}Sn_{0.9}O_{12}$.

zation measurements[9]. It can be seen from Fig. (b) that in the temperature dependence of the width of the Fe^{57} spectra there is a weakly pronounced "tail" in the temperature region above T_N.

C. Spectra of the Sn^{119} Nuclei

It is known that in the magnetically-ordered region a large magnetic field, reaching ~200 kOe, acts on the Sn^{119} nuclei in the Ferrite-garnets[7-11]. In this case the total width of the split Zeeman spectrum of Sn^{119} in this region is approximately three times greater than the total width of the Fe^{57} spectrum[15]. In the paramagnetic region of temperatures the Mössbauer spectrum of the Sn^{119} nuclei in the garnets investigated consists of a single, somewhat broadened line. At high enough temperatures the value of the linewidth is constant (see Fig. (a)). As the temperature is lowered the linewidth begins to increase smoothly at a temperature about 20—30 degrees above T_N, and then increases sharply at the point T_N itself, just as happens with the spectra of the Fe^{57} nuclei.

DISCUSSION

The observed tail in the linewidth of the Sn^{119} spectra indicates, apparently, that the tin nuclei continue to feel, as it were, the magnetic order in the garnet in a certain temperature range above T_N, while the iron nuclei are almost insensitive to it. This result can hardly be explained by invoking arguments about the inhomogeneity of the samples, as this would entail a certain distribution of Néel points. In this case the tails ought to be observed both in the spectra of the Sn^{119} nuclei and in the Fe^{57} spectra. Moreover, they ought to be more weakly pronounced for the tin nuclei. The point is that the magnetic field at the nuclei of the diamagnetic tin ions is due to covalent mixing of 3d- and 5s-orbitals in the chain of chemical bonds Fe-O-Sn[11] and, in the first approximation, reflects the magnetic state of the iron ions closest to the tin. But these ions possess weakened exchange couplings, since they have at least one diamagnetic ion in their immediate vicinity[8]. In this case, the field at the Sn^{119} nuclei ought to vanish at temperatures that are in any case not higher than the ordering temperature of the iron ions. In addition, the complete absence of any additional peaks in the Sn^{119} and Fe^{57} spectra at low temperatures speaks in favor of the good homogeneity of the samples.

It might be supposed that the line-broadening of the Sn^{119} spectra is associated with quadrupolar effects due to a certain structural phase transition before the Néel point is reached, leading to a change in the local distortions at the octahedral sites. However, in this case the quadrupolar splitting would also be observed in the magnetically-ordered region, in contradiction with experiment. Moreover, the quadrupole moment of the Sn^{119} nuclei is considerably smaller than that of the Fe^{57} nuclei. Therefore, in the case of structural changes, quadrupolar effects would be manifested more strongly in the Fe^{57} spectra. This is also not observed experimentally.

Thus, we can assume, evidently, that the observed features of the Sn^{119} spectra are associated with a certain magnetic interaction which the nuclei of the diamagnetic tin atoms begin to feel at temperatures 20—30° above T_N.

It is interesting to compare the relative magnitudes of the effective fields $H(T)/H(0)$ at the Sn^{119} and Fe^{57} nuclei that correspond to the broadening of the lines of the tin and iron spectra. Under certain conditions, these quantities are proportional to the mean magnetization[16]. An estimate of this value for tin shows that, at the Néel point,

$$H^{Sn}(T_N)/H^{Sn}(0\text{K}) \approx 0.025 \pm 0.002.$$

There is no field at the iron nuclei in the paramagnetic region of temperatures. An estimate of the errors in the measurement gives the condition:

$$H^{Fe}(T_N)/H^{Fe}(0\text{K}) \leqslant 0.007 \pm 0.002.$$

A possible cause of the presence of tails in the temperature dependence of the linewidth of the Sn^{119} spectra could be effects associated with fluctuations of the magnetic moments near the temperature T_N. In this case, as in the case of paramagnetic relaxation[17], the form of the Mössbauer spectra is determined by the relationship between the Larmor precession frequency ω_L of the nuclear spins in the effective magnetic field, and the characteristic frequency ω_F of the fluctuations of the magnetic moment of the ion, which depends strongly on the temperature and is, generally speaking, unknown. The condition for observation of the magnetic hyperfine splitting in Mössbauer spectra is $\omega_F \lesssim \omega_L$.

Using our data on the magnitude of the magnetic fields at the tin and iron nuclei in these garnets[10,18], we have calculated the Larmor frequencies for the Sn^{119} and Fe^{57} nuclei. It was found that for the tin nuclei the frequency ω_L is two to four times greater than for the iron nuclei. This means that an effective magnetic field should be observed at the tin nuclei in the presence of more rapid fluctuations of the spins or at higher fluctuation frequencies than it is at the iron nuclei. In this case the tails in the temperature dependence of the width of the spectra should be more clearly pronounced in the case of Sn^{119}.

However, such a small difference in the Larmor frequencies (less than an order of magnitude) may be insufficient for a full explanation of the observed effect. Another hypothesis may also be put forward. Up to now, we have assumed that the characteristic spin-fluctuation frequencies ω_F are the same for the iron and tin atoms. It is possible, however, that the covalent effects that lead to transfer of spin density from iron ions to tin ions in the garnets impose further conditions on the frequencies ω_F, so that the relaxation processes at the tin are slowed down. It is possible, e.g., to assume that the local crystal field at an octahedral site occupied by a tin ion perturbs the orbital angular momentum in such a way that only electrons with a certain preferred spin orientation are transferred from the iron to the electron shell of the tin (on account of spin-orbit interaction effects). This creates a nonzero mean magnetic moment on the tin, whereas on the iron it has time to be averaged to zero.

In this case the effects that we have observed should give additional information on the anture of the indirect exchange interaction between the paramagnetic iron ions and the diamagnetic tin ions, and on the mechanism of the transfer of spin density from the iron to the tin.

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