

Magnetic fields at the nuclei of diamagnetic tin atoms in the spin glass Fe_2TiO_5

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(Submitted 22 April 1992)

Pis'ma Zh. Eksp. Teor. Fiz. **55**, No. 11, 642–645 (10 June 1992)

The transition of the oxide Fe_2TiO_5 into a spin-glass state has been studied by Mössbauer spectroscopy of the nuclei of diamagnetic tin impurity atoms. This transition cannot be described by the model of a uniaxial magnetic disorder. A method is proposed for extracting the temperature of the transition to the spin-glass state, T_g , from Mössbauer-spectroscopy data.

Atzmony *et al.*¹ have reported that at $T_g \approx 55$ K the nonconducting oxide Fe_2TiO_5 goes into a state with a magnetic disorder which is “frozen” along the short c axis. That report has stimulated several other studies^{2–7} of this compound, which Atzmony *et al.*¹ called an “anisotropic spin glass.”

The compound Fe_2TiO_5 (pseudobrookite) has an orthorhombic unit cell (space group $Cmcm$; $a = 9.79$, $b = 9.93$, $c = 3.72$ Å) in which, according to x-ray diffraction,⁸ the Fe^{3+} and Ti^{4+} ions occupy $8f$ and $4c$ octahedral sites, respectively. The FeO_6 octahedron is substantially distorted. However, Mössbauer spectroscopy of ^{57}Fe nuclei has revealed a localization of Fe^{3+} ions in both $8f$ and $4c$ sites.⁹ This result has been confirmed by neutron diffraction. On the other hand, neutron diffraction has not detected a long-range magnetic order in pseudobrookite down to $T = 4.2$ K (the spin correlations between nearest iron ions are preserved up to $T \approx 650$ K). The random nature of the distribution of magnetic ions (Fe^{3+}) and nonmagnetic ions (Ti^{4+}) in the $8f$ and $4c$ sites of the pseudobrookite structure results in a frustration of the bonds responsible for exchange interactions. It also leads to the transition to a spin-glass state.^{1–6,10} This assertion can finally be regarded as an established fact now,⁴ on the basis of the irreversible behavior of the magnetization as a sample is cooled in a zero field. It was reported in Refs. 4, 5, and 7 that, in addition to the longitudinal ($\parallel c$) freezing in Fe_2TiO_5 , there is apparently also a transverse ($\perp c$) freezing, at $T \approx 6$ K.

In this letter we are reporting a study of powdered pseudobrookite samples by Mössbauer spectroscopy of ^{119}Sn and ^{57}Fe nuclei (4.2–300 K); the ^{119}Sn was added in a concentration of 1% by mass. Since the tin ions do not have an intrinsic electron magnetic moment, the hyperfine magnetic field H_{hf} at the ^{119}Sn nuclei is determined

primarily by direct and indirect contributions from the nearest magnetic neighbors (the indirect contributions are made through oxygen ions). Accordingly, H_{hf} is sensitive primarily to the number and configuration of the bonds with such neighbors (Fe^{3+} ions). It follows that information obtained on ^{119}Sn nuclei can be of substantial help in filling in the picture of the transition of Fe_2TiO_5 into a spin-glass state.

The test samples were prepared by the standard ceramic procedure (Ref. 2, for example) and were checked by x-ray diffraction. The ^{57}Fe spectra turned out to be similar to those found in Refs. 1-3, 6, and 9; this agreement, combined with the x-ray diffraction results, is evidence that the samples consisted of a single phase.

The characteristics of the spectrum of ^{119}Sn nuclei at room temperature [an isomer shift $\delta = 0.124(2)$ mm/s with respect to SnO_2 , a quadrupole splitting $\Delta = 0.434(3)$ mm/s, and a linewidth $G = 0.796(4)$ mm/s] are typical of the Sn^{4+} ion in an octahedral coordination, with slight distortions of the oxygen polyhedron of SnO_6 . It can therefore be assumed that the tin ions (in contrast with the Fe^{3+} ions) occupy only $4c$ sites in the pseudobrookite structure.

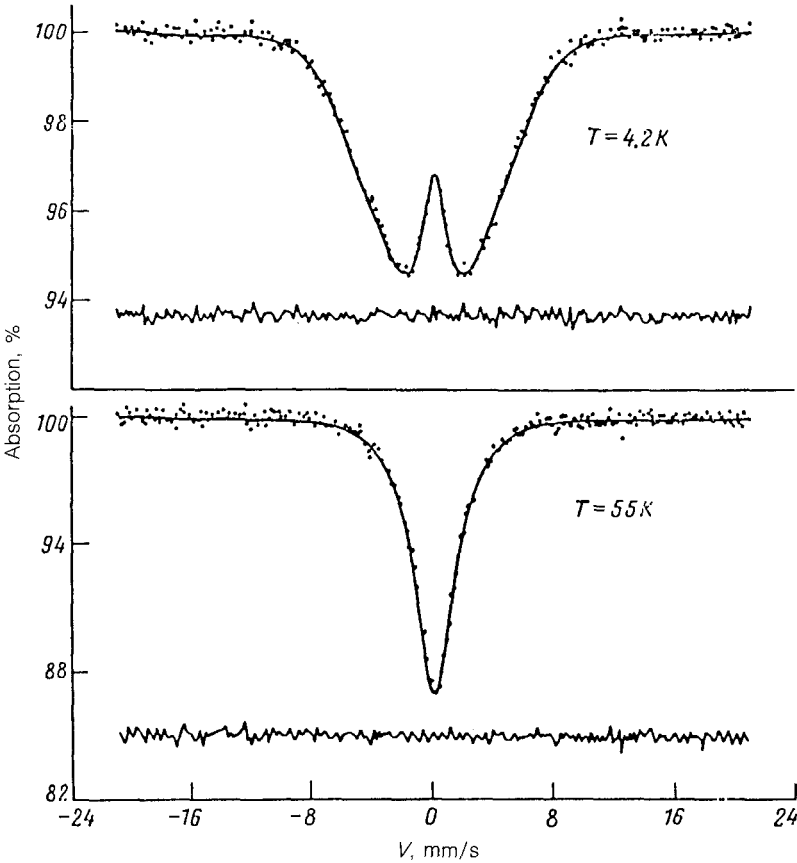


FIG. 1. Mössbauer spectra of ^{119}Sn nuclei in a Fe_2TiO_5 sample; the ^{119}Sn concentration is 1% by mass.

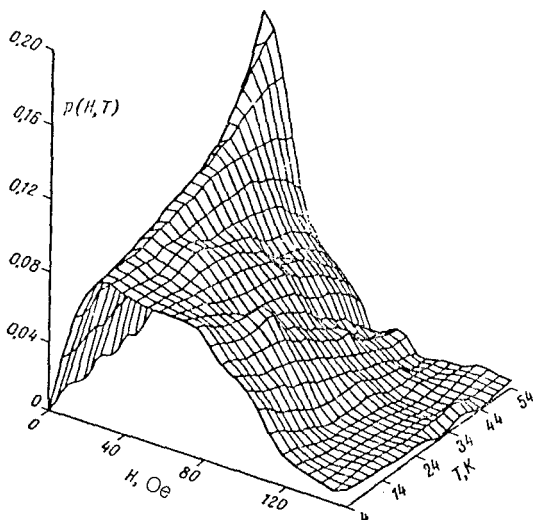


FIG. 2. The $p(H_{hf}, T)$ surface for ^{119}Sn nuclei.

The ^{119}Sn spectrum ($T = 4.2$ K; Fig. 1) has a broad, symmetric doublet and is the result of a superposition of unresolved components of the magnetic hyperfine structure with various values of H_{hf} . At $T_g = 55$ K (Fig. 1) the spectrum transforms into a visually unresolved doublet, differing from that found at $T + 300$ K only in being wider. The results were analyzed with the help of the DISTRI program, which constructs the distribution function of the properties of the spectrum, in this case, $p(H_{hf})$. This program is based on a version of the regularization method in which one can make use of *a priori* information on the distribution function. During the reconstruction of $p(H_{hf})$, a search is made for linear correlations among H_{hf} , δ , and $\epsilon = \Delta/2$.

Figure 2 shows a $p(H_{hf}, T)$ surface constructed from curves of $p(H_{hf}, T_i; i = 1-10)$, each consisting of 21 points. The absence of contributions to $p(H_{hf}, T_i)$ from $H_{hf} = 0$ at low temperatures and the increase in these contributions as $T \rightarrow T_g$ can be regarded as characteristic features of this distribution. The temperature dependence of the mean field, $\bar{H}_{hf}(T)$, and that of the standard deviation $S[p(H_{hf})]$ (the width of the distribution is W) are shown in Fig. 3a. In contrast with the results³ on ^{57}Fe nuclei, the value of W found for ^{119}Sn nuclei increases, rather than decreases, with decreasing T . This behavior indicates that $p(H_{hf}^{\text{Sn}})$ is being affected primarily by the various configurations of the nearest neighborhood of the Sn^{4+} ion, rather than by relaxation, in the pseudobrookite structure.

The curves of the transmission intensity $I(T)$ (Fig. 3, b and c) found by temperature scanning in the single-channel regime for ^{119}Sn and ^{57}Fe nuclei reflect the dynamics of the "pumping" of magnetic hyperfine structure into paramagnetic structure in the Fe_2TiO_5 spectra. In other words, these curves actually span the entire temperature range of the transition of the system to a spin-glass state, if this transition is viewed from the standpoint of the measurement time characteristic of Mössbauer spectroscopy.

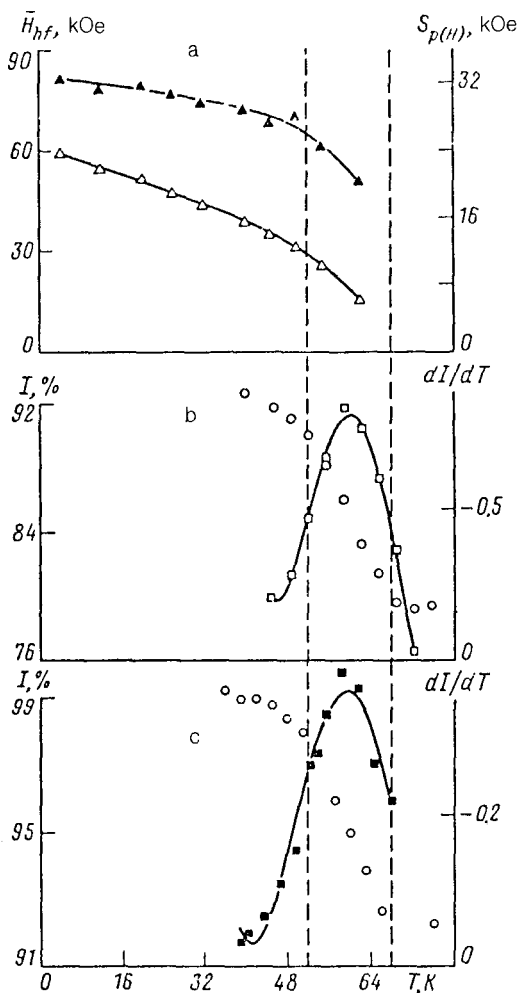


FIG. 3. Temperature dependence of various properties. a—The mean field \bar{H}_{hf} (\blacktriangle) and the standard deviation $S_p(H)$ (\triangle) found from $p(H_{hf}, T)$ for ^{119}Sn nuclei; b, c— $I(T)$ and dI/dT , respectively, for ^{119}Sn and ^{57}Fe nuclei. The dashed lines show the half-width of $dI/dT(T)$.

py,¹⁾ $\tau_m \approx 10^{-7}$ – 10^{-8} s. For quantitative estimates of T_g it is convenient to introduce the derivative dI/dT , found through a numerical differentiation, followed by a fit by a fourth-degree polynomial (Fig. 3, b and c). The extrema of dI/dT can then be related in a natural way with the transition temperatures, $T_g = 58$ and 60 K for ^{119}Sn and ^{57}Fe , respectively. These figures are slightly higher than the values $T_g = 55$ (Ref. 1), 48 (Ref. 5), and 49 K (Ref. 7) which have been found from measurements of the dynamic magnetic susceptibility χ_T and the magnetization^{5,7} $M(T)$. The scatter in the values of the transition temperature is a consequence of a dependence of this temperature on the measurement time (τ_m) characteristic of the given experimental method.

The temperature T_g falls off slowly with increasing τ_m . Using the results on $T_g = f(\tau_m)$ from Ref. 5, found from data on M ($\tau_m \approx 10^2$ – 10^4 s), χ_T ($\tau_m \approx 10^{-2}$ – 10^{-4} s), and neutron diffraction ($\tau_m \approx 10^{-10}$ – 10^{-11} s), and making the substitution $\tau_m = \tau_L$ in them for ^{119}Sn and ^{57}Fe nuclei, we find $T_g = 60$ and 62 K, respectively. These figures are close to our estimates of T_g from the derivative dI/dT .

As we mentioned earlier, there are no contributions from $H_{hf} = 0$ in the distribution $p(H_{hf}, T)$ at low temperatures. Using a binomial distribution, we calculated the probabilities for possible magnetic configurations of the nearest neighborhood of the Sn^{4+} ion in the $4c$ site of the Fe_2TiO_5 structure for the case $M(\text{Fe})\parallel c$. We took account of the indirect-exchange mechanisms. All bonds responsible for exchange interactions were equivalent. In this case the contribution to $p(H_{hf})$ from zero fields is $> 8\%$. In this case the dependence of H_{hf} on the bond configuration (Ref. 11, for example) could not have a strong effect solely on the estimate of the $H_{hf} = 0$ contribution.

In summary, the transition of pseudobrookite into a spin-glass state cannot be described by the model of a uniaxial magnetic disorder. A more likely model is one in which each spin deviates a certain angle α from c axis, and the set of spins forms a conical distribution around c . We might note that a transverse component corresponds to the second and fifth components of the magnetic hyperfine structure in the ^{57}Fe spectra found from single-crystal samples,^{1,3} as was pointed out in Ref. 12.

¹The lifetime of the excited states of the ^{57}Fe nucleus is $\tau_e = 10^{-7}$ s, and that of the ^{119}Sn nucleus is $\tau_e = 2 \times 10^{-8}$ s. In order to observe the magnetic hyperfine structure, however, it is necessary to satisfy the conditions $\omega_L \tau_e > 1$ and $\omega_L \tau_R > 1$, where ω_L is the frequency of the Larmor precession of the magnetic moment of the nucleus in the field H_{hf} , and τ_R is a time scale of the fluctuations in H_{hf} . In the region $T_g \approx 55$ K, we have $\tau_L \approx 2.5 \times 10^{-8}$ s and $\omega_L \tau_e \approx 3$ for ^{119}Sn ($\overline{H}_{hf} = 25$ kOe), and we have $\tau_L \approx 1.4 \times 10^{-8}$ s and $\omega_L \tau_e \approx 30$ for ^{57}Fe ($\overline{H}_{hf} = 200$ kOe).

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Translated by D. Parsons