Evidence of dipole spin glass in magnetically dilute dielectric $CaF_2:Er^{3+}$

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(Submitted 29 July 1980)
Pis'ma Zh. Eksp. Teor. Fiz. **32**, No. 7, 461–464 (5 October 1980)

A formation of spin glass due to magnetic dipole interaction between impurity ions was observed for the first time in the investigation of magnetic susceptibility in CaF_2 crystals with a 1% impurity of Er^{3+} ions (effective spin $S' = 1/2$) at temperatures below 0.8 K.

PACS numbers: 75.30.Cr, 75.30.Hx

The state in which spin magnetic moments randomly distributed in a solid are "frozen" in randomly oriented, local fields, in the absence of macroscopic magnetization of the material, is called spin glass. An interest in this problem increased dramatically after a sharp maximum was discovered in the temperature dependence of the magnetic susceptibility of the AuFe alloy. This was interpreted as evidence of a phase transition from the paramagnetic state to spin glass.[1] The number of theoretical and experimental papers dealing with this subject now numbers in the hundreds; however, no universally accepted definition of spin glass yet exists (see, for example, Ref. 2).

The interaction responsible for the formation of spin glass in metals is the long-

range RKKI exchange potential, whose sign oscillates rapidly as a function of the distance r_{ij} between the interacting spins and which attenuates as r_{ij}^{-3}. One of the authors pointed out[3] the analogy between this potential and the magnetic dipole-dipole interaction, which also decreases proportionally to r_{ij}^{-3}, and whose sign oscillates as a function of the orientation of the vector $\mathbf{r}_{ij}$. It was concluded[3] on this basis that spin glass can exist in magnetically dilute dielectrics with a dipole interaction. Subsequently, the question of dipole spin glass was discussed in several theoretical papers (see, for example, Ref. 4); however, this phenomenon has not been observed until now.

The relatively weak dipole interactions, which correspond (for reasonable concentration of paramagnetic impurity $c \sim 1\%$) to a hard-to-achieve transition temperature $T_f \lesssim 10^{-2}$ K, were the major obstacle to an experimental search for dipole spin glass. To avoid this difficulty, it was suggested[3] to reduce the temperature of the dipole subsystem by using the method of "adiabatic demagnetization in a rotating coordinate system", i.e., the method previously used to obtain nuclear magnetic ordering.[5] The difficulties that arise when this idea is applied to electron spins forced us to choose another approach, namely, to select a system with an anomalously high value of the g factor of the paramagnetic impurity (we remind that the dipole-dipole energy is proportional to g^2).

The CaF_2 crystals with Er^{3+} ions as impurity were chosen as this material. When these crystals are grown by a special method, the impurity ions, which replace the Ca^{2+}, give an EPR spectrum that can be characterized by a slightly anisotropic g factor with components[6] $g_{\parallel} = 7.76$ and $g_{\perp} = 6.25$. This made it possible to expect an increase of T_f of more than an order of magnitude as compared with the normal paramagnetic materials in which $g = 2$.

It is crucial that the effective spin S' of an Er^{3+} ion is equal to 1/2, and the natural content of the only odd ^{167}Er isotope amounts to only 23%. This ensures the absence of low-temperature susceptibility anomalies, which can arise due to electric or hyperfine splitting of the energy levels of a paramagnetic ion. We note that such anomalies in the 10^{-1}–10^{-3} K range can influence the evaluation of the results obtained using Eu^{2+} (Refs. 7–9), Ho^{3+} (Ref. 10), and other ions.

Finally, there is reason to assume that the exchange interaction between the nearest Er^{3+} neighbors in CaF_2 is small compared with the dipole interaction: the latter is of the order of 1 K, whereas the exchange energy in such a CaF_2:Nd^{3+} system does not exceed 0.15 K.[11]

Our experiment involved the measurement of the real part of the magnetic susceptibility χ' at a frequency $\nu \approx 330$ kHz in a zero constant magnetic field and in the temperature range $T = 0.07$–2.2 K. The value of χ' was measured from the frequency shift of a tunnel-rectifier oscillator that operated at helium temperatures (the long-term stability was about 1 Hz). The amplitude of the variable magnetic field surrounding the sample did not exceed 2 A/m. A solution refrigerator using an ^{3}He-^{4}He mixture was used to cool the sample.

The results of measurements for a sample with an Er^{3+} concentration $c = 1\%$ (relative to Ca^{2+}) are shown in Fig. 1. We can see that at temperatures below $T_f \approx 0.8$ K the Curie law is replaced by a decrease in the χ' value, which continues to

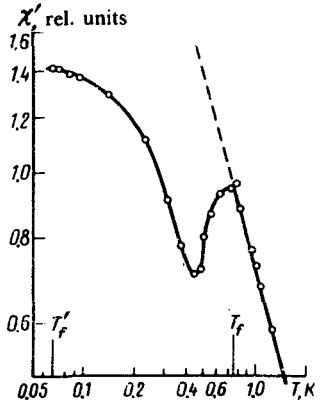

FIG. 1. Temperature dependence of the magnetic susceptibility in $CaF_2:Er^{3+}$. The straight line is the Curie law.

about 0.45 K. With further cooling, we again observe an increase in the susceptibility, which shows a tendency to saturate (or to reach a new maximum?) near $T_f' \approx 0.07$ K.

The dependence in Fig. 1 is very similar to the results obtained using $SrS:Eu^{2+}$ samples for $c < 10\%$.[7,8] According to these papers, the susceptibility maximum at $T = T_f$ should be regarded as a result of the temperature dependence of the longitudinal spin-spin relaxation time τ_S, which, as suggested, increases sharply with cooling and reaches values of the order of $1/2\pi\nu \approx 5 \times 10^{-7}$ sec near T_f (note that a high temperatures $\tau_S \approx 5 \times 10^{-10}$ sec for our sample). We emphasize, however, that the interpretation suggested in Refs. 7 and 8 is based on the presence of a strong short-range exchange interaction in $SrS:Eu^{2+}$ that results in the formation of superparamagnetic clusters, and , in addition, it uses a Eu^{2+} spin that is greatly different from 1/2. Both of these conditions cannot be used in our case, to say nothing of the fact that the role of clusters can hardly be considered important at low concentration of the paramagnetic centers used by us.

Another assumption is that the formation of the dipole spin glass occurs at $T = T_f$; however, this state is unstable down to temperatures of the order of $T_f' \approx 0.07$ K, competes with the paramagnetic phase, and finally becomes dominant at $T < T_f'$. We note that the given T_f' value is in good agreement with the rms dipole local field, which is equal to about 0.1 cm^{-1} in this case (see Ref. 3). It is clear, however, that the final interpretation will be possible after additional experiments, which will make it possible to determine the frequency, concentration, and field dependences of the magnetic susceptibility.

The authors thank L. D. Livanova and I. N. Kurkin for providing the crystals used in the experiments.

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Translated by Eugene R. Heath
Edited by S. J. Amoretty