MAGNETISM
AND FERROELECTRICITY

Spin Glass State in Crystals of Barium Ferrigermanate $Ba_2Fe_2GeO_7$

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Received January 10, 2006

Abstract—The temperature dependence of the magnetization and elastic neutron scattering spectra of $Ba_2Fe_2GeO_7$ barium ferrigermanate polycrystals are studied. The magnetization is found to depend on the magnetic prehistory of a $Ba_2Fe_2GeO_7$ sample below $T = 8$ K. Analysis of the neutron scattering spectra does not reveal long-range magnetic order down to 2 K. Our experimental data indicate the existence of a spin glass state in $Ba_2Fe_2GeO_7$ polycrystals.

1. INTRODUCTION

Tetragonal barium ferrigermanate $Ba_2Fe_2GeO_7$ is a representative of the family of compounds having the structure of the melilite $Ga_2Al_2SiO_7$ and crystallizing in the space group $P\bar{4}2_1m$ ($Z = 2$) [1, 2]. Lyubutin et al. [1] were the first to synthesize polycrystals of this compound by a solid-phase reaction at a temperature $T = 1200°C$. In our recent work [3], we studied the magnetic and structural properties of barium ferrigermanate and showed that, in terms of its magnetic properties, the crystal lattice of this compound can be considered two-dimensional.

The structure of barium ferrigermanate is formed by layers that alternate along the c tetragonal axis and consist of polyhedra containing barium ions (Thomson cubes) and two types of oxygen tetrahedra joined into five-membered rings (Fig. 1). Larger sized, comparatively regular tetrahedra $T1$, which have symmetry $\bar{4}$ and are located at vertices and at the center of the bases of the tetragonal cell, are occupied by Fe^{3+} ions. Less regular tetrahedra $T2$, which form diortho groups $[M_2O_7]$ with symmetry $mm2$, are randomly occupied by Fe^{3+} and Ge^{4+} ions approximately in a 1 : 1 ratio. All magnetic ions are predominantly coupled by antiferromagnetic exchange interaction. As was shown in [3], the distribution of Fe^{3+} and Ge^{4+} over the tetrahedral positions $T2$ plays an essential role in the formation of a magnetic structure of ferrigermanate layers. The temperature dependence of the magnetic susceptibility of $Ba_2Fe_2GeO_7$ crystals exhibits a feature at $T = 8$ K that

is characteristic of transitions to a magnetically ordered state. In [3], the need for additional studies aimed at determining the magnetic structure of $Ba_2Fe_2GeO_7$ at low temperatures was stressed.

We report here on a further study of the magnetization and elastic neutron scattering spectra of the $Ba_2Fe_2GeO_7$ barium ferrigermanate.
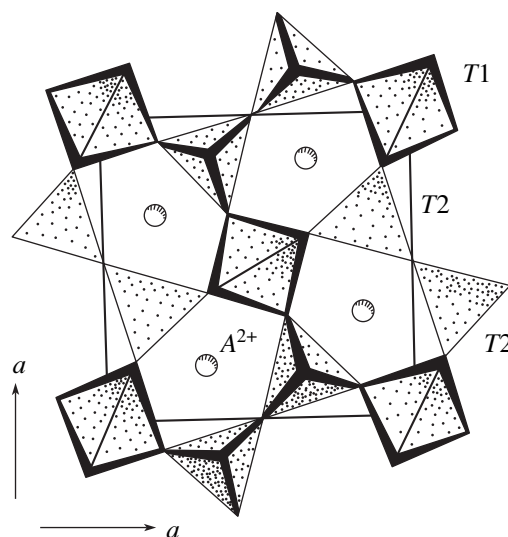

Fig. 1. Crystal structure of the barium ferrigermanate $Ba_2Fe_2GeO_7$ in the projection onto the (001) plane. $A^{2+} = B^{2+}$.

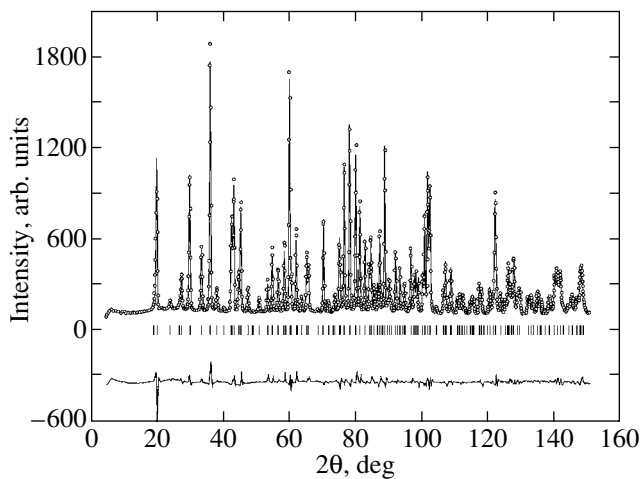**Fig. 2.** Theoretical (points) and experimental (solid line) elastic neutron scattering spectra of a $Ba_2Fe_2GeO_7$ poly-crystal at $T = 2$ K.

Fig. 3. Temperature dependences of the magnetization measured for a $Ba_2Fe_2GeO_7$ single crystal during cooling in magnetic fields of (*1*) 100 and (*3*) 30 Oe and (*2*, *4*) without a magnetic field.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

The preparation procedure and crystal structure of single-crystal barium ferrigermanate $Ba_2Fe_2GeO_7$ were described earlier in [3].

The neutron scattering spectra were measured using a powder sample prepared from thoroughly ground single crystals. The measurements were performed on a D1A setup ($\lambda = 1.911$ Å) at the Laue–Langevin Institute (Grenoble, France) in a zero magnetic field at temperatures ranging from 2 to 20 K.

The temperature dependences of the magnetization were measured on a SQUID magnetometer in the temperature range 4.2–30.0 K and in magnetic fields (up to 100 Oe) applied perpendicular to the c crystal axis.

3. EXPERIMENTAL RESULTS

The neutron scattering spectra measured at temperatures of 2 K (below) and 20 K (above the specific feature in the temperature dependence of the susceptibility [3]) turned out to be identical. Figure 2 presents the model (points) and experimental (solid curve) neutron scattering spectra recorded at $T = 2$ K. The model spectrum was calculated only for neutron scattering from ions of the crystal structure without any magnetic peaks. Also shown is the difference between the two neutron scattering spectra, which indicates the absence of additional (magnetic) peaks in the experimental neutron diffraction pattern.

In our opinion, the above findings can be explained by two factors. The first factor is the fairly small magnetic moment of the Fe^{3+} ion, which precludes measurement of the magnetic peaks, if there are any. This situation appears, i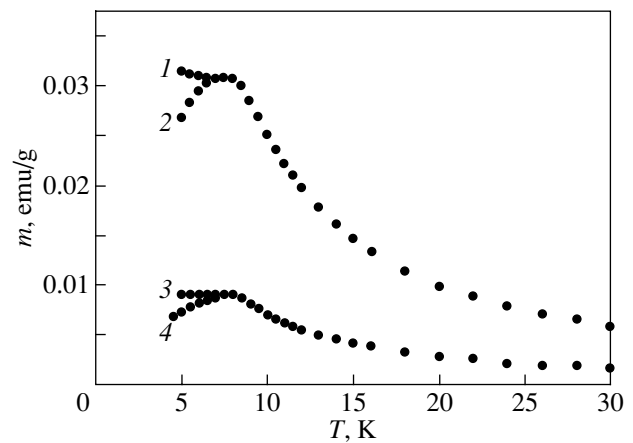n principle, quite possible. The second factor is the absence of long-range magnetic order in the compound under study at low temperatures. However, the specific feature observed in the temperature dependence of the magnetic susceptibility at $T = 8$ K [3] argues convincingly for the sample not remaining paramagnetic down to $T = 2$ K.

To clarify this point, we measured the magnetization of a $Ba_2Fe_2GeO_7$ single crystal cooled in different magnetic fields and with no field applied. The results obtained are presented in Fig. 3.

It was found that the magnetization of the sample strongly depends on the cooling conditions at temperatures below 7.5 K in a magnetic field of 30 Oe and below 7 K in a field of 100 Oe.

4. DISCUSSION OF THE RESULTS

The absence of magnetic peaks in the neutron scattering spectra and the dependence of the magnetization of a sample on its magnetic prehistory are characteristic of the spin glass state [4, 5]. However, the spin glass state, as a rule, is observed in amorphous magnetic materials and metallic alloys. A prerequisite for the existence of a spin glass is the presence of frustrated exchange interactions, as well as their random distribution over the crystal lattice. Earlier [3], we established that the Curie–Weiss temperature Θ for $Ba_2Fe_2GeO_7$ is negative in sign. This implies that antiferromagnetic exchange interactions dominate in the $Ba_2Fe_2GeO_7$ compound. Assuming the Curie–Weiss temperature Θ to be determined by the exchange interaction J of the nearest neighbors ($z = 4$) and using the relationship $\Theta = -zJS(S + 1)/3k_B$, we obtain $J = -0.6$ K for the exchange interaction of the nearest neighbor ions Fe^{3+}. It should be emphasized that the obtained value is the average exchange interaction in the system. Moreover, if the

exchange interactions are antiferromagnetic, they are totally frustrated. It was also established in [3] that, owing to the random distribution of Fe^{3+} and Ge^{4+} ions over the $T2$ positions, these interactions are randomly distributed over the crystal lattice. A similar situation was observed earlier in a $CuGa_2O_4$ crystal [4].

5. CONCLUSIONS

Thus, the experimental data obtained allow the conclusion that, at temperatures below 8 K, the $Ba_2Fe_2GeO_7$ crystal can be in the spin glass state.

ACKNOWLEDGMENTS

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Translated by G. Skrebtsov