Physics of the Solid State, Vol. 47, No. 11, 2005, pp. 2114–2118. Translated from Fizika Tverdogo Tela, Vol. 47, No. 11, 2005, pp. 2027–2031.

MAGNETISM
AND FERROELECTRICITY

Synthesis and Properties of Barium Ferrigermanate $Ba_2Fe_2GeO_7$

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Received March 2, 2005

Abstract—The magnetic susceptibility and specific heat of single crystals of the $Ba_2Fe_2GeO_7$ barium ferrigermanate are investigated. It is revealed that the temperature dependence of the magnetic susceptibility exhibits a kink at a temperature $T = 8.5$ K. The number of nonequivalent positions of Fe^{3+} ions and their occupancies are determined using Mössbauer spectroscopy. It is shown that the Fe^{3+} ions located in tetrahedral positions $T2$ are ordered incompletely, which is inconsistent with the results obtained previously. An assumption is made regarding the possible ground magnetic state of the $Ba_2Fe_2GeO_7$ compound. *© 2005 Pleiades Publishing, Inc.*

1. INTRODUCTION

Magnetic systems whose structure contains tetragonal layers with antiferromagnetic exchange interactions can exhibit interesting properties, such as order by disorder (with complete frustration of the exchange interactions in the layer) [1] and a spin-singlet state due to the modification of the structure through magnetoelastic coupling [2]. It is worth noting that an important role in this case is played by quantum magnetic fluctuations. The situation is complicated when the system is characterized by a considerable covalency of bonding, i.e., when different spin states of paramagnetic ions become possible due to the violation of the Hund rule. Similar effects can be observed, for example, in a melilite structure [3] with paramagnetic ions.

It should be noted that, in the physics of polyfunctional materials, single crystals with a combination of different magnetic and electrical properties have particularly attracted the attention of researchers. For example, tetragonal copper metaborate, which is of interest from the standpoint of the nontrivial type of magnetic ordering [4], exhibits a piezoelectric effect comparable in magnitude to that of quartz [5]. Similar properties can be expected for other magnetically ordered crystals. In the present work, we synthesized and investigated the properties of single crystals of tetragonal barium ferrigermanate $Ba_2Fe_2GeO_7$ [3]. The barium ferrigermanate undergoes melting with decomposition, and single crystals of this compound have not been grown to date.

In this work, we grew barium ferrigermanate single crystals using the solution–melt method and analyzed the first results of an experimental investigation into its magnetic properties, specific heat, and Mössbauer effect.

2. CRYSTAL STRUCTURE OF BARIUM FERRIGERMANATE

Tetragonal barium ferrigermanate $Ba_2Fe_2GeO_7$ is a representative of the family of compounds that have a structure of the melilite ($Ca_2Al_2SiO_7$) type and crystallize in the space group $P\bar{4}2_1m$ ($Z = 2$) [3, 6]. Polycrystals of this compound were first synthesized by the solid-phase reaction at a temperature $T = 1200°C$ [3]. The structure of the barium ferrigermanate is built up of 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 relatively 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 predominantly occupied by Fe^{3+} ions. Less regular tetrahedra $T2$, which form diortho groups $[M_2O_7]$ with symmetry $mm2$, are statistically occupied by Fe^{3+} and Ge^{4+} ions approximately in a 1 : 1 ratio. The structural formula, which accounts for the distribution of cations over crystallographic positions $T1$ and $T2$, can be approximately written in the form $Ba_2(Fe^{3+})_{T1}(Fe^{3+}Ge^{4+})_{T2}O_7$. This distribution of Fe^{3+} cations over tetrahedral positions $T1$ and $T2$ was determined using Mössbauer spectroscopy for polycrystalline samples [3]. Among the compounds synthesized to date in the melilite family and belonging to the same structural type, the $Ba_2Fe_2GeO_7$ barium ferrigermanate is characterized by the highest iron content and is most

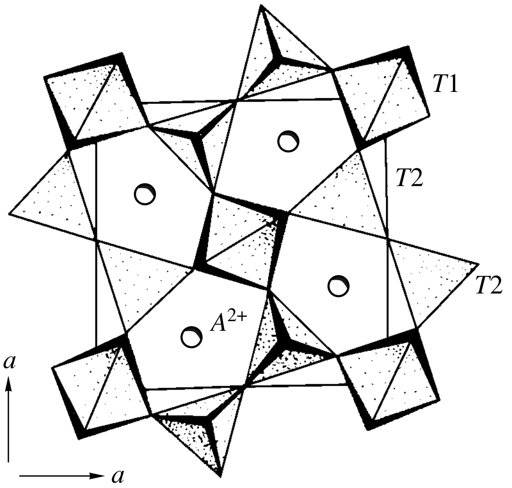

Fig. 1 Structure of the melilite crystal as projected onto the (001) plane. $A^{2+} = Ba^{2+}$ or Sr^{2+}.

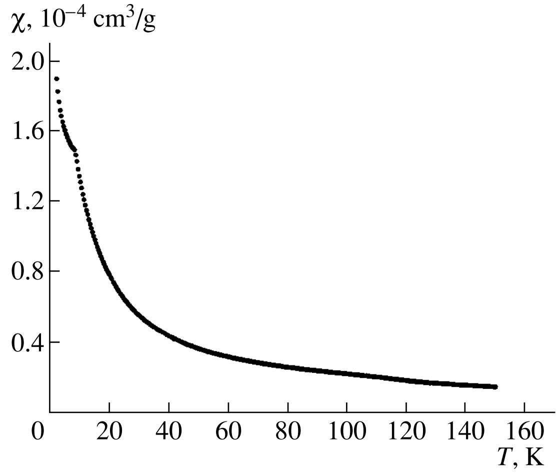

Fig. 2. Temperature dependence of the real part of the magnetic susceptibility at a frequency of 1000 Hz in a magnetic field of 10 Oe.

attractive for use in magnetic investigations. As regards the magnetic properties, it is important to note that Fe^{3+} ions form square planes perpendicular to the *c* crystallographic axis in such a way that the Fe^{3+} ion is located at the center of each square formed by the Fe^{3+} ions. In the case when the exchange interactions in each plane are antiferromagnetic in nature, they are frustrated completely. This prevents manifestation of a long-range antiferromagnetic order. Consequently, the exchange interactions between far neighbors play an important role. Moreover, the so-called mechanism of attainment of order by disorder due to the nonlinear interaction of magnetic excitations in the frustrated spin system [1] can also make a significant contribution.

3. EXPERIMENTAL TECHNIQUE, RESULTS, AND DISCUSSION

3.1. Crystal Synthesis

This paper reports on the results of the first investigations into the crystal structure and the magnetic, thermal, and electrical properties of barium ferrigermanate single crystals. The crystals were grown by the solution–melt method with the use of a PbF_2–B_2O_3-based solution melt containing 68 wt % ($PbF_2 + 0.62B_2O_3 + 1.09BaO + 0.45GeO_2$) and 32 wt % $Ba_2Fe_2GeO_7$. In this system, $Ba_2Fe_2GeO_7$ is the high-temperature phase (T_{sat} = 940°C) and, in the range of its stability, is represented in a binary form. The density of the solution melt is higher than that of the barium ferrigermanate, and the growth was performed in a weakly nonuniform temperature field at $dT/dh < 0$ ($|dT/dh| \leq 2$ K/cm) according to the Kyropoulos method. Black single crystals of the compound had the shape of rectangular plates (4 × 6 × 2 mm).

The X-ray diffraction investigations confirmed that the crystal grown has a helenite structure with the tetragonal unit cell parameters a = 8.33 Å and c = 5.59 Å. The lattice parameters of the crystals grown and the polycrystals synthesized by the solid-phase reaction [3] are in good agreement. This indicates that partial substitution of Pb^{2+} for Ba^{2+} due to the ion exchange $PbF_2 + BaO \rightleftharpoons PbO + BaF_2$ does not occur under the above conditions of crystal growth.

3.2. Magnetic Susceptibility and Specific Heat

The magnetic and thermal measurements were performed on a PPMS setup and a SQUID magnetometer. The complex magnetic susceptibility was measured in the temperature range 2–150 K at a frequency of 1 kHz in a magnetic field of 10 Oe, which was directed both perpendicular and parallel to the *c* axis. The results of the measurements are presented in Fig. 2.

It can be seen from Fig. 2 that, at a temperature of approximately 8.5 K, the temperature dependence of the magnetic susceptibility exhibits a kink, which is characteristic of transitions to a magnetically ordered state. The anisotropy of the magnetic susceptibility manifests itself at temperatures below 30 K. It should be noted that the temperature dependence of the reciprocal of the magnetic susceptibility can be separated into three linear portions (13 K < T < 45 K, 60 K < T < 100 K, 120 K < T < 150 K) with different slopes and, hence, with different Curie–Weiss temperatures. This can be associated with the retention of exchange-coupled fragments of the magnetic structure at intermediate temperatures. The fitting at temperatures higher than 120 K results in the Curie–Weiss temperature $\theta = -6.7$ K and the effective magnetic moment $\mu_{eff} = 2.3\mu_B$, where μ_B is the Bohr magneton. This magnetic moment differs substantially from the theoretical value of the

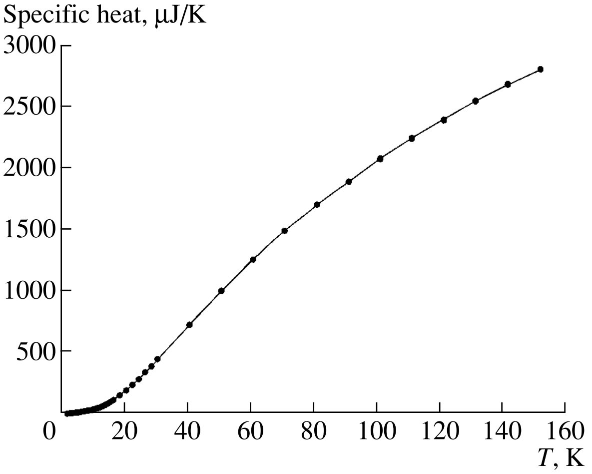

Fig. 3. Temperature dependence of the specific heat for the $Ba_2Fe_2GeO_7$ crystal.

magnetic moment (5.92 μ_B) for Fe^{3+} ions. The Curie–Weiss temperature is negative and, hence, the antiferromagnetic exchange interactions are dominant in the studied compound. Under the assumption that the Curie–Weiss temperature θ is determined by the exchange interaction J of the nearest neighbors $z = 4$, the exchange interaction between the nearest neighbors of the Fe^{3+} ions (i.e., $J = -0.6$ K) is determined from the relationship $\theta = -zJS(S + 1)/3k_B$. It should be emphasized that the obtained value corresponds to the average exchange interaction in the system. Since all the exchange interactions in the plane are antiferromagnetic and frustrated, the calculated exchange integral can appear to be considerably underestimated.

The experimental temperature dependence of the specific heat in the temperature range 2–14 K is plotted in Fig. 3. Note that this dependence does not exhibit a noticeable feature at temperatures close to 9 K. A similar situation was also observed for the Ca_3CoRhO_6 compound and was explained by the smearing of the magnetic phase transition [7]. However, this effect is still not clearly understood.

The $Ba_2Fe_2GeO_7$ crystal is a good insulator.

3.3. Mössbauer Investigation

The analysis of the crystal structure of the ferrihelenite revealed that the spacing between layers containing structure-forming tetrahedra is rather large. The distance between the nearest anions of the adjacent layers is greater than 3 Å. The Ba–O distance is approximately equal to 2.5 Å. These large distances allow us to ignore the exchange interaction between cations of the adjacent layers. Within this approximation, the ferrihelenite lattice can be considered a two-dimensional lattice from the standpoint of magnetism.

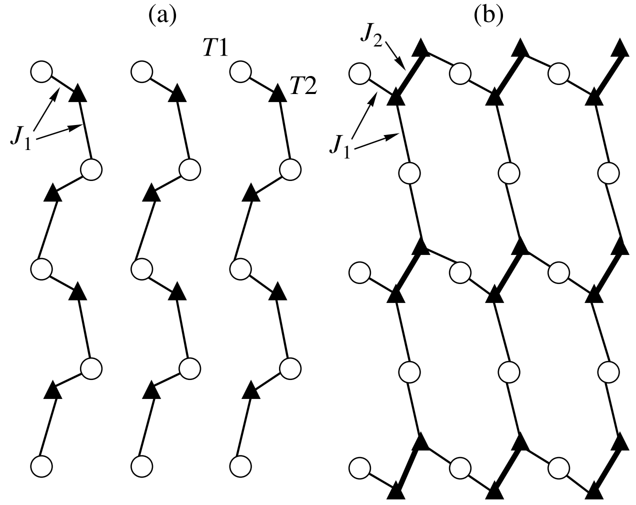

Fig. 4. Ordering of Fe^{3+} and Ge^{4+} ions over the *T*2 positions of helenite.

Large-sized weakly distorted tetrahedra *T*1 form two simple tetragonal lattices inserted into each other. More strongly distorted tetrahedra *T*2 are joined in pairs. These pairs also form two simple tetragonal lattices inserted into each other. One lattice is located above and the other lattice is positioned below the plane formed by *T*1 tetrahedra. In the ferrihelenite structure, the *T*1 tetrahedra are occupied only by Fe^{3+} cations, whereas the *T*2 tetrahedra are occupied by Fe^{3+} and Ge^{4+} cations in a 1 : 1 ratio.

From analyzing the cation–cation exchange interactions in the framework of the simple model of indirect coupling [8, 9], we obtained the following relationships:

$$\begin{aligned} J_1(\mathrm{Fe}^{3+}(T1) - \mathrm{Fe}^{3+}(T2)) &= -6a^2U\cos 45°/25, \\ J_2(\mathrm{Fe}^{3+}(T2) - \mathrm{Fe}^{3+}(T2)) &= -24a^2U/75, \end{aligned} \qquad (1)$$

where a is the parameter of ligand–cation electronic transfer, which is equal to the square of the coefficient characterizing the admixture of the ligand wave function to the cation wave function; U is the energy of cation–ligand electronic excitation; and the cosine roughly describes the angular dependence of the transfer integral. It follows from relationships (1) that the exchange interaction J_2 is nearly twice as strong as the exchange interaction J_1.

The distribution of Fe^{3+} and Ge^{4+} cations over the *T*2 tetrahedral positions plays an important role in the formation of the magnetic structure of ferrihelenite layers. By assuming that cations of different types are ordered in the *T*2 tetrahedral positions, we can consider two possible variants.

(i) A pair of *T*2 cations is formed by cations of different types (Fe^{3+}, Ge^{4+}). In this case, we obtain zigzag chains along one of the a axes, as is shown in Fig. 4a, where circles indicate Fe^{3+} cations in the $T1$ tetrahedral positions and triangles represent Fe^{3+} cations in the $T2$ tetrahedral positions. Since the exchanges for each cation to the right and to the left along the chain are equivalent, the chains are magnetically homogeneous. For this type of ordering, the (a, a, c) lattice should transform into the (a, b, c) lattice due to the difference between the radii of the Fe^{3+} and Ge^{4+} cations.

(ii) A pair of $T2$ cations is formed by cations of the same type (layer-by-layer ordering). In this case, we have antiferromagnetic pairs of Fe^{3+} cations. These pairs are coupled with each other in two directions through the interaction with $T1$ cations, thus forming a two-dimensional lattice. This type of ordering is illustrated in Fig. 4b. Since $J_2 > J_1$, we can expect the formation of antiferromagnetic dimers, which are in a singlet state and, hence, cannot be magnetically coupled with the surrounding matrix. The matrix is the sublattice of Fe^{3+} cations ($T1$) that are not bonded to each other. Consequently, this sublattice is in a quasi-paramagnetic state. Therefore, in the case of ordering of the second type, we have an ensemble of antiferromagnetic dimers Fe^{3+} ($T2$) in the paramagnetic lattice of Fe^{3+} ions ($T1$). In this situation, the helenite lattice can undergo an orthorhombic distortion.

The above analysis clearly demonstrates that, in the case when the Fe^{3+} and Ge^{4+} cations are statistically distributed over the $T2$ positions, the helenite layer involves a set of magnetically different objects, namely, single paramagnetic cations, singlet pairs, finite homogeneous chains, and two-dimensional regions.

The Mössbauer spectrum measured for a powder of the single crystal is fairly well approximated by two doublets. The doublet parameters listed in Table 1 (where IS is the isomer shift with respect to α-Fe, QS is the quadrupole splitting, W is the absorption line width at half-maximum, and S is the fractional occupancy of the cation position) are in qualitative agreement with the results obtained for polycrystalline samples in [3]. The considerably larger values of the isomer shift and quadrupole splitting in [3] are most likely associated with the defect structure of polycrystals. The isomer shift is characteristic of Fe^{3+} ions in the tetrahedral environment, and the large value of the quadrupole splitting indicates a strong distortion of this environment.

In order to reveal the possible ordering of cations over the $T2$ positions in the ferrihelenite structure, the Mössbauer spectra were identified in two stages. At the first stage, we determined the distribution functions of the quadrupole splitting $P(QS)$ for two valence states of iron. For this purpose, the Mössbauer spectrum was represented as the sum of two groups of doublets with the isomer shifts given in Table 1 and natural width of the absorption line. The quadrupole splitting was varied in steps of 0.05 mm/s. The distribution functions $P(QS)$ were determined by varying the amplitudes of doublets and the isomer shifts that were identical for each group of doublets. The distribution functions $P(QS)$ thus obtained are presented in Fig. 5.

Table 1. Parameters of the Mössbauer spectrum of barium ferrigermanate

Position	IS, mm/s	QS, mm/s	W, mm/s	S
$T1$	0.205	1.117	0.413	0.497
$T2$	0.187	1.525	0.337	0.503

The maxima in the distribution functions $P(QS)$ indicate that the helenite structure can involve additional iron positions that are nonequivalent in terms of the degree of local distortion. The information obtained from the distribution functions $P(QS)$ is qualitative in character, because these functions were determined using identical isomer shifts for each group of doublets. In the general case, this can lead to the appearance of false maxima.

At the second stage of the identification of the Mössbauer spectra, we constructed a model spectrum on the basis of the number and approximate values of the parameters estimated for the nonequivalent positions from the distribution functions $P(QS)$. The model spectrum was fitted to the experimental spectrum by varying the entire set of hyperfine parameters with the use of the least-squares procedure in the linear approximation. In the course of this fitting, the desired parameters are refined and the occupancies of positions that are responsible for the doublets corresponding to the false maxima become negligible. The results of the two-stage identification of the Mössbauer spectra are presented in Table 2.

The revealed nonequivalent positions, namely, three $T1$ and two $T2$ positions, can be assigned to the positions with different numbers of nearest cations of a particular type. In the case when the $T2$ positions are half occupied, the most probable configuration of the four

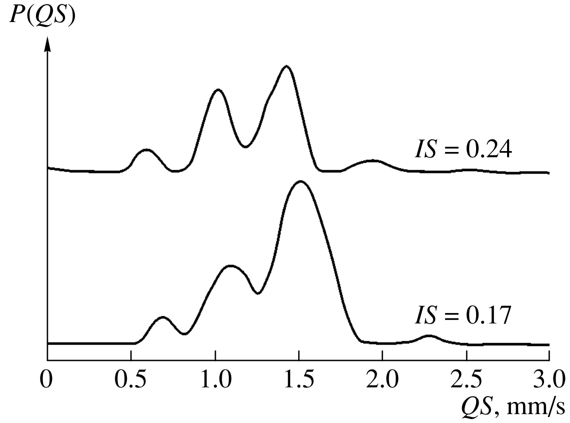

Fig. 5. Distribution functions of the quadrupole splitting $P(QS)$ for two valence states of iron ions in barium ferrigermanate.

Table 2. Mössbauer parameters of the nonequivalent positions of iron ions in barium ferrigermanate

Position	*IS*, mm/s	*QS*, mm/s	*W*, mm/s	*S*	Nearest neighbor configuration	Occupation probability for a random distribution
	0.204	0.711	0.251	0.060	3Fe1Ge	0.125
*T*1	0.223	1.038	0.268	0.065	1Fe3Ge	0.125
	0.230	1.403	0.361	0.355	2Fe2Ge	0.1875
*T*2	0.163	1.201	0.432	0.253	3Fe	0.25
	0.159	1.571	0.312	0.267	2Fe1Ge	0.25

nearest neighbors for the *T*1 position is the 2Fe2Ge configuration. This is the sole configuration when the cations are ordered over the *T*2 positions. The appearance of the 3Fe1Ge and 1Fe3Ge configurations indicates a random distribution of Fe^{3+} and Ge^{4+} cations over the *T*2 positions.

Of the three neighbors of the *T*2 position, two are always represented by Fe^{3+} cations occupying the *T*1 positions. The third neighbor is a Ge^{4+} cation in the case of ordering. For a random distribution, the Fe^{3+} or Ge^{4+} cation can equiprobably serve as the third neighbor; i.e., the presence of nonequivalent positions *T*2 counts in favor of the random distribution. Therefore, the structure of the barium ferrigermanate can be treated from the standpoint of magnetism as built up of magnetically different objects (from isolated paramagnetic cations to two-dimensional regions). It is worth noting that the occupancies of the cation positions with the revealed configurations differ significantly from their occupation probabilities for the actual random distribution of cations (see the last column in Table 2). These differences are larger than the experimental error and may suggest a partial ordering of Fe^{3+} and Ge^{4+} cations over the *T*2 positions.

4. CONCLUSIONS

A tetragonal crystal of the $Ba_2Fe_2GeO_7$ melilite was grown for the first time. The distribution of Fe^{3+} cations over nonequivalent tetrahedral positions in the crystal lattice was determined using Mössbauer spectroscopy. The temperature dependence of the magnetic susceptibility was measured. The presence of three linear portions in the temperature dependence of the reciprocal of the magnetic susceptibility and the small effective magnetic moment can serve as indirect evidence that the magnetic structure of the $Ba_2Fe_2GeO_7$ compound involves singlet pairs, finite homogeneous chains, and two-dimensional regions, which are characterized by specific effective exchange interactions and are sequentially ordered with a decrease in the temperature. The observed feature in the temperature dependence of the magnetic susceptibility at $T = 8.5$ K can be associated with the manifestation of a long-range magnetic order in the system.

The temperature dependence of the specific heat does not exhibit an anomalous behavior at the point of the magnetic phase transition. This finding is not clearly understood. Possibly, this can be explained by the specific features of the transition to the magnetically ordered state.

At present, we intend to perform experiments on inelastic neutron scattering in order to elucidate the type of magnetic ordering in the $Ba_2Fe_2GeO_7$ compound.

ACKNOWLEDGMENTS

This work was supported by the Division of Physical Sciences of the Russian Academy of Sciences, project no. 2.1.1.2.

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Translated by O. Borovik-Romanova