Acoustic anomaly in Fe_3BO_6

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We study the acoustic anomaly in the region of the Γ_2–Γ_4 orientational phase transition in Fe_3BO_6 and discover its nonstandard feature, namely, that as the speed of sound decreases, the ultrasound amplitude at the phase transition point grows. The speed of transverse sound propagating along the **a** axis of the crystal does not depend on the polarization of the sound in the (**bc**) plane. Comparative analysis of magnetic-resonance and acoustic experiments supports the assumption that the phase transition in Fe_3BO_6 is intermediate in nature between first- and second-order phase transitions, and in this sense is unique and of interest for studies of the important problem concerning the nature of the "magnetoelastic gap" in magnetic materials.

1. INTRODUCTION

When studying the dynamics of orientational phase transitions (OPTs) in magnetic materials there is always the question of the role of the magnetoelastic (ME) interaction as formulated in the works of Borovik-Romanov and Rudashevskiĭ[1] and Lida and Tasaki,[2] that is, the nature of what is known as the magnetoelastic gap. Such a gap emerges in the system of the interacting fields of a crystal as a result of spontaneously broken symmetry (spontaneous strain), is universal for all magnetically ordered crystals, manifests itself, for one thing, in the presence of an energy gap in the spectrum of a softening magnetoresonance mode, and essentially is of general physical interest.[3]

A large body of experimental data concerning this question have been gathered near second-order OPTs. A number of orthoferrites $RFeO_3$, where R=Yb, Tm, Er, Ho, Sm, and Nd have been used for a comparative analysis of the magnetoelastic-gap effect. These orthoferrites have a characteristic $\Gamma_2(G_z,F_x)$–$\Gamma_4(G_x,F_z)$ OPT, which proceeds as two second-order phase transitions: Γ_2–Γ_{24} and Γ_{24}–Γ_4. Here **G** is the antiferromagnetism vector, and **F** the vector of weak ferromagnetism of iron. Together with experiments involving magnetic-resonance methods, direct acoustic measurements are gaining ever growing acceptance.

The Fe_3BO_6 crystal, like all orthoferrites, is orthorhombic and is characterized by a Γ_2–Γ_4 OPT. However, this is the only known orthorhombic crystal in which the spin reorientation from one weakly ferromagnetic state to another occurs through a first-order phase transition. Hence the interest of researchers. Magnetic-resonance studies of the dynamics of spontaneous spin reorientation in Fe_3BO_6 have shown[4,5] that further studies are needed in order to understand this phase transition. Here for the first time the results of investigating the spontaneous phase transition in Fe_3BO_6 by acoustic methods are presented and a comparative analysis is made with the data from magnetic-resonance experiments.

2. THE EXPERIMENTAL METHOD

The necessary measurements were done using a pulsed ultrasound spectrometer. The acoustic vibrations were excited by a resonant lithium-niobate piezoelectric transducer, which ensured the generation of purely longitudinal or transverse acoustic modes with a frequency f=25–30 MHz. Measurements of sound attenuation were conducted in the continuous regime and written by an automatic recording instrument. Relative measurements of the speed of sound were conducted via the point phase-sensitive method. At room and liquid nitrogen temperatures the observed number of reliably resolved ultrasonic echo-pulses passing through the sample was 12 and 6 for the longitudinal acoustic mode $\mathbf{q}\|\,\boldsymbol{\varepsilon}\|\,\mathbf{a}$, 20 and 10 for the transverse acoustic mode $\mathbf{q}\|\,\mathbf{a}$ and $\boldsymbol{\varepsilon}\|\,\mathbf{c}$, and 30 and 10 for the transverse acoustic mode $\mathbf{q}\|\,\mathbf{a}$ and $\boldsymbol{\varepsilon}\|\,\mathbf{b}$ (here **q** is the acoustic wave vector and $\boldsymbol{\varepsilon}$ is the vector specifying the direction of polarization of the transverse ultrasonic wave), which made it possible to reliably determine the absolute speed of sound in the crystal.

The phase transition point T lies at about 415 K. This requires thermal isolation of the active volume from the piezoelectric transducers. Hence, the sample was placed between two 4-cm-long delay lines manufactured from Z-cut quarts. Acoustic contact between the delay lines and the sample was secured through an aluminum foil 7-μm thick by pressing together rather strongly the flat surfaces, without using any acoustic grease. Acoustic contact between the delay lines and the piezoelectric transducers, which were maintained at room temperature, was secured through an aluminum foil via a common grease of the GKZh brand. The sample was a $6.4\times3.1\times1.02$ mm plane-parallel plate, with the normal vector **n** parallel to the single-crystal axis **a**. The accuracy with which **a** coincided with **n** was roughly 0.5°, and the accuracy with which sound polarization plane was adjusted in the sample's plane was roughly 3°.

3. RESULTS AND DISCUSSION

1. According to theoretical calculations,[4] at the phase transition point the curve representing the temperature de-

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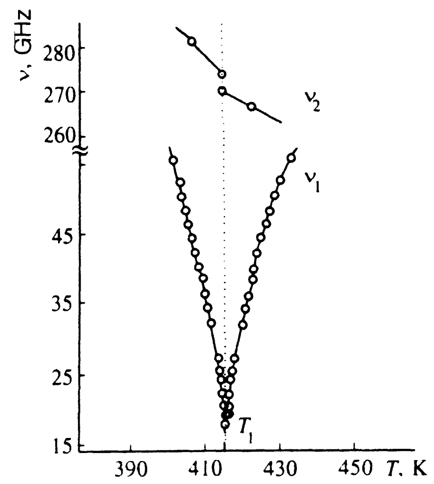

FIG. 1. Temperature dependence of the magnetic-resonance frequencies of the ferromagnetic (ν_1) and antiferromagnetic (ν_2) branches in Fe_3BO_6 in spin reorientation.

pendence of the high-frequency quasiantiferromagnetic mode ν_2 experienced a break $\Delta\nu = \nu_2(\Gamma_2) - \nu_2(\Gamma_4)$, while for the low-frequency quasiferromagnetic mode $\nu_1(T)$ at the phase transition point $\nu_1(\Gamma_2) = \nu_1(\Gamma_4)$, this branch softens completely, and the respective energy gap is nil. In other words, the theory states that Fe_3BO_6 is characterized by a spontaneous first-order phase transition, which in its nature, however, borders on a second-order phase transition.

Experimental magnetic-resonance studies of the dynamics of this phase transition in a broad frequency range[4,5] did indeed show that at $T = T_1$ for mode ν_2 there is a jump in frequency of the order of the predicted one ($\Delta\nu \sim 4$ GHz), while the frequencies of mode ν_1 for phases Γ_2 and Γ_4 coincide at this point to within experimental errors. However, the experiment firmly established the presence of a sizable energy gap (~ 17.5 GHz) in the spectrum of the ν_1 mode (Fig. 1).

This contradiction suggests that a finite energy gap in the case of a first-order phase transition is caused by the fact that the anisotropy energy and, correspondingly, the magnetic-resonance frequency in a first-order phase transition do not vanish. For a second-order phase transition the anisotropy energy is zero, and a finite energy gap is caused by various interactions between the vibrational subsystems of the crystal (spin, elastic, electromagnetic, etc.; see Refs. 1–3) or the contribution of longitudinal oscillations of magnetization.[6]

If an ordinary first-order phase transition occurs in Fe_3BO_6, near it there should be a temperature interval of phase lability (a mixed state). According to the estimates in Ref. 5, the lability temperatures for the Γ_2 and Γ_4 phases are 419 K and 410 K, respectively. If the intermediate phase transition is realized, the phase-lability interval vanishes and the observed energy gap actually occurs for the reasons given above, which are characteristic of a second-order phase transition.

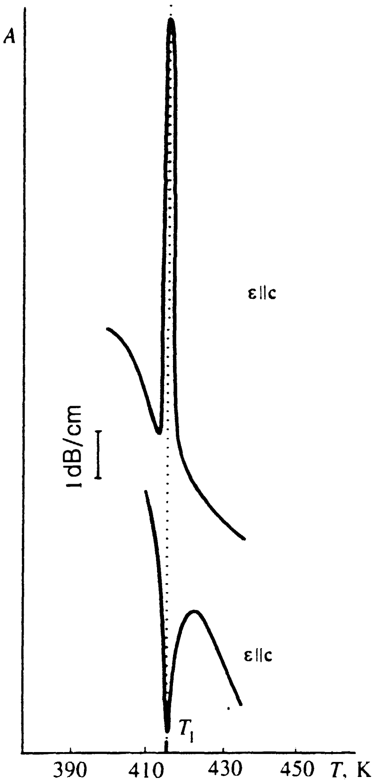

FIG. 2. Temperature dependence of the amplitude of transverse acoustic modes passing through the sample, in the neighborhood of a spontaneous phase transition in Fe_3BO_6.

There is hope that the nature of this phase transition can be clarified by acoustic measurements.

2. The results of ultrasonic measurements are represented in Fig. 2. Note that until recently the behavior of the absorption and speed of a quasiacoustic wave in the vicinity of an OPT in $ErFeO_3$ (Refs. 7–12), $TmFeO_3$ (Refs. 9 and 13), $HoFeO_3$ (Ref. 14), and $YbFeO_3$ (Ref. 15) always agreed qualitatively with the existing theoretical ideas (see, e.g., Ref. 7). For instance, the respective active acoustic mode (active in the sense of interacting with the magnon mode) is characterized for both Γ_2–Γ_{24} and Γ_{24}–Γ_4 transitions by the presence of critical resonance-type anomalies in the speed and attenuation of ultrasound. Varying considerably in magnitude, width, and shape, the anomalies, nevertheless, were characterized by a fixed decrease in speed accompanied by a decrease in amplitude of the ultrasonic signal. The behavior of the other acoustic modes also agreed with the one predicted by theory for second-order OPT.

Symmetry analysis shows that the sonic wave active in our experiment was the one whose strain tensor contained the U_{xz} component transformed as the order parameter of the Γ_2–Γ_4 phase transition, that is, the transverse acoustic mode with $\mathbf{q} \| \mathbf{a}$ and $\varepsilon \| \mathbf{c}$ or with $\mathbf{q} \| \mathbf{c}$ and $\varepsilon \| \mathbf{a}$. Figure 2 depicts the results of measuring the amplitude of the ultrasonic signal that passed through the sample and delay lines, with the geometry of the experiment being $\mathbf{q} \| \mathbf{a}$ and $\varepsilon \| \mathbf{c}$. The desired effect superposed on the smooth variation with temperature of the main measured quantities owing to the variation in the signal caused by its passage through the quartz delay lines. The experiment has shown the following: (a) the speed anomaly (the relative variation of the speed of sound, $\Delta S/S$, amounted to roughly 0.2%) and sound attenuation anomaly are represented by resonance-like curves; (b) the speed and sound-attenuation anomalies rigidly correspond to each other on the temperature scale; (c) the width of the observed acoustic anomaly (at its base) amounts to 5–8 K, considerably exceeding the one observed, for instance, in $\mathrm{ErFeO_3}$ (see Ref. 12), and approximately coinciding with the region where phases Γ_2 and Γ_4 coexist, estimated in Ref. 5; and (d), which is most remarkable, at the phase transition point $T=T_1$ the amplitude of the ultrasonic signal increases (rather than decreases, as in all orthoferrites) with decreasing speed of sound.

The inactive ultrasonic wave with $\mathbf{q}\parallel\mathbf{a}$ and $\boldsymbol{\varepsilon}\parallel\mathbf{b}$ also manifests a resonance-like anomaly, but at $T=T_1$ the amplitude of the signal decreases (see Fig. 2). To within experimental errors no speed variations in this geometry have been observed.

3. Measurements at $T=293$ K of the speed of sound in the $\mathrm{Fe_3BO_6}$ single crystal under investigation yielded the following results:

- longitudinal: $S^{\parallel}_{\mathbf{q}\parallel\mathbf{a}}=8.16\times10^5$ cm s^{-},
- transverse: $S^{\perp}_{\mathbf{q}\parallel\mathbf{a},\boldsymbol{\varepsilon}\parallel\mathbf{b}}=4.30\times10^5$ cm s^{-1},
- transverse: $S^{\perp}_{\mathbf{q}\parallel\mathbf{a},\boldsymbol{\varepsilon}\parallel\mathbf{c}}=4.30\times10^5$ cm s^{-1}.

The values of the speed of sound at $T=77$ K were

- longitudinal: $S^{\parallel}_{\mathbf{q}\parallel\mathbf{a}}=8.29\times10^5$ cm s^{-1},
- transverse: $S^{\perp}_{\mathbf{q}\parallel\mathbf{a},\boldsymbol{\varepsilon}\parallel\mathbf{b}}=4.32\times10^5$ cm s^{-1},
- transverse: $S^{\perp}_{\mathbf{q}\parallel\mathbf{a},\boldsymbol{\varepsilon}\parallel\mathbf{c}}=4.32\times10^5$ cm s^{-1}.

Note the extraordinary fact that to within experimental errors the speed of the transverse ultrasonic wave remains unchanged under an arbitrary variation of its direction of polarization in the (**bc**) plane.

4. CONCLUSIONS

Analysis of the experimental data leads to the following conclusions.

1. Acoustic measurements set the finite temperature of the mixed-state region at a value ($\leqslant 10$ K) coinciding with that estimated from magnetic-resonance experiments. Together with the observed jump for the ν_2 mode this signifies that the observed phase transition is first-order.

2. The peculiar behavior of the acoustic anomaly (the increase, at $T=T_1$, of the amplitude of the active ultrasonic signal passing through the sample and the resonant, rather than step-like, variation of the speed of sound) and the symmetry (noticed in both types of experiments) of the region of lability of phases Γ_2 and Γ_4 with respect to the phase transition point $T=T_1$ point to the need to consider the phase transition in fact to be close in nature to a second-order phase transition.

3. The above suggests that the spontaneous phase transition in $\mathrm{Fe_3BO_6}$ is intermediate in nature between first- and second-order phase transitions, and the energy gap for ν_1 is caused primarily by the interaction of the different vibrational subsystems, which is characteristic of a second-order phase transition.

4. The peculiar feature of the transition is apparently also due to the nonstandard, that is, independent of $\boldsymbol{\varepsilon}$, behavior of the absolute value of the speed of transverse sound with $\mathbf{q}\parallel\mathbf{a}$ under variations of the sound's polarization in the (**bc**) plane.

A final conclusion about the nature of this phase transition can be drawn after a thorough theoretical analysis of the entire body of the experimental data.

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