

## Letters to the Editor

### CHANGE OF RESONANCE ABSORPTION SPECTRA OF 23.8-keV GAMMA RAYS OF $\text{Sn}^{119}$ DURING PHASE TRANSITIONS OF THE $\text{BiFeO}_3\text{-Sr}(\text{Sn}_{1/3}\text{Mn}_{2/3})\text{O}_3$ SYSTEM

K. P. MITROFANOV, A. S. VISKOV, G. Ya. DRIKER, M. V. PLOTNIKOVA, PHAM ZUY HIEN, Yu. N. VENEVTSEV, and V. S. SHPINEL'

Nuclear Physics Institute, Moscow State University; L. Ya. Karpov Physico-chemical Institute

Submitted to JETP editor September 27, 1963

J. Exptl. Theoret. Phys. (U.S.S.R.) **46**, 383-386 (January, 1964)

SOLID solutions based on the ferroelectric-antiferromagnetic  $\text{BiFeO}_3$  (with Curie point  $T_C = 850$  and Néel point  $T_N = 370^\circ\text{C}$ <sup>[1,2]</sup>) are convenient objects for studying ferroelectricity and "ferro-antiferromagnetism." The compound  $\text{BiFeO}_3$  has the perovskite structure and forms a series of solid solutions of this same structure with stannates of elements of Group II. The presence of tin in these compounds enables us to apply the method of recoilless resonance absorption of the 23.8-keV  $\text{Sn}^{119}$   $\gamma$  rays to determine the nature of the binding of the tin atoms and the crystalline fields acting on them. Combined with data from measurements of magnetic and electric properties of these compounds and the results of x-ray analysis, the  $\gamma$  ray absorption results can give information about the nature of the changes in crystals during phase transitions leading to the appearance of special electric and magnetic properties.

The first results of a study of a similar system  $\text{BiFeO}_3\text{-SrSnO}_3$  have already been reported.<sup>[3]</sup> We noted an anomaly in the change of the effect  $\epsilon$  with temperature: at certain temperatures there was an abrupt change in  $\epsilon$ , the smaller  $\epsilon$  occurring in the lower temperature region (as usual  $\epsilon$  denotes the % change in counting rate at the absorption maximum). The widths of the resonance absorption lines were the same at temperatures below and above the region where the abrupt change in the effect occurred.

The points where the abrupt change in the effect occurred were identified with the values of the Curie temperature, and the "jump" was considered to be the result of a change in the Mössbauer probability  $f'$  during a ferroelectric phase transi-

tion. But there also seemed to be some discrepancy between the resonance absorption results and the data from high temperature x-ray photographs, from which the ferroelectric phase transition temperature  $T_C$  was determined.

The main purpose of the present work was to improve these results and find the reasons for the abrupt change in  $\epsilon$ . The investigation was made on samples of the system  $\text{BiFeO}_3\text{-Sr}(\text{Sn}_{1/3}\text{Mn}_{2/3})\text{O}_3$ , which has properties close to those of the system studied earlier.<sup>[3]</sup> Adding Mn made it possible to obtain samples which were practically single phase and closer to equilibrium. The measurements of resonance absorption of  $\gamma$  rays were done with equipment using a constant speed, and the detector was a resonant counter.<sup>[4]</sup> The use of the resonant counter made possible measurements with very high accuracy, which is especially important in determining small effects.

The work was done with a  $\text{Sn}^{119\text{m}}$  source in the form of  $\text{SnO}_2$ , having the same characteristics as in <sup>[3]</sup>. The source was kept at room temperature for all the measurements, while the absorber temperature could be varied smoothly from  $-190$  to  $500^\circ\text{C}$ . Samples were used in which the fraction of the tin-containing component varied from 10 to 60 mol%. The absorption spectra of these samples, as for other compounds of this type where the tin ions are surrounded octahedrally by oxygens, is a single line located close to the null velocity value relative to  $\text{SnO}_2$ .

The magnitude of the effect was determined from the dip at zero velocity relative to the counting rate of "recoilless"  $\gamma$  quanta at large absorber velocities  $v$ :

$$\epsilon_0 = (N_\infty - N_0) / (N_\infty - N_b).$$

Here  $N_\infty$  and  $N_0$  are the counting rates for absorber velocities 4 mm/sec and zero, while  $N_b$  is the counting rate for "nonresonant"  $\gamma$  quanta (a velocity of 4 mm/sec is sufficiently large compared to the width of the absorption line to be regarded as infinite). To determine  $N_b$  one must destroy the resonance between source and absorber, which is easily done by vibrating the source. The level of the nonresonant background depends on the absorber thickness. When working with thin absorbers  $N_b$  is 15-20% of the value of  $N_\infty$ . Figure 1 shows the temperature variation of  $\epsilon_0$  for a few compositions. An interesting feature is the complete disappearance of the effect when the sample is cooled below certain definite temperatures. The curves are like the analogous curves for the system  $\text{BiFeO}_3\text{-SrSnO}_3$ ,<sup>[3]</sup> with

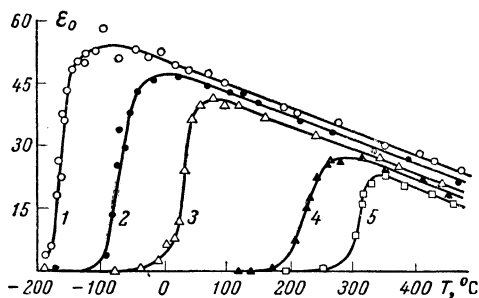


FIG. 1. Dependence of effect  $\epsilon_0$  on temperature for solid solutions based on  $\text{BiFeO}_3$ , for different content of tin-containing component. Curves 1-5 correspond to 40, 50, 61.5, 80 and 90 mol%  $\text{BiFeO}_3$ .

the one difference that the effect drops to zero on cooling and the transition region is much narrower. From these results we construct a diagram (Fig. 2) showing the temperature where  $\epsilon_0$  changes rapidly as a function of composition. Extrapolating to pure  $\text{BiFeO}_3$ , we get  $T = 380-400^\circ$ , which corresponds to the antiferromagnetic transition temperature.

The points in Fig. 2 correspond to the middle of the "jump" for the different samples. The result of the extrapolation is not changed if one chooses some other characteristic point in the region of rapid change of  $\epsilon_0$ . If the origin of the anomalous change of  $\epsilon_0$  is magnetic in nature, then as the temperature is lowered, together with the drop in the effect one should see a change in the absorption spectrum caused by the Zeeman splitting of the nuclear levels. To check this point we made a detailed study of the spectrum from  $-20$  mm/sec to  $+20$  mm/sec. The measurements were made on samples prepared using tin oxide enriched to 75% in  $\text{Sn}^{119}$ .

Figure 3 shows the results of measurements on an absorber in which there was 38.5% of the tin-containing component, at three different temperatures:  $+160$ ,  $+23$ , and  $-196^\circ\text{C}$ . We see that as the temperature is lowered the single line disappears, giving way to a broad distribution which can be interpreted to be a strongly smeared Zeeman spectrum. The total area of the spectrum is approximately equal to the area under the absorption line

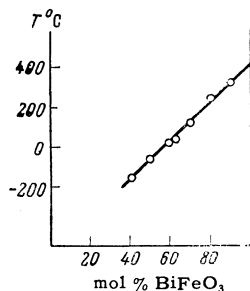


FIG. 2. Dependence of phase transition temperature on molar concentration of  $\text{BiFeO}_3$ .

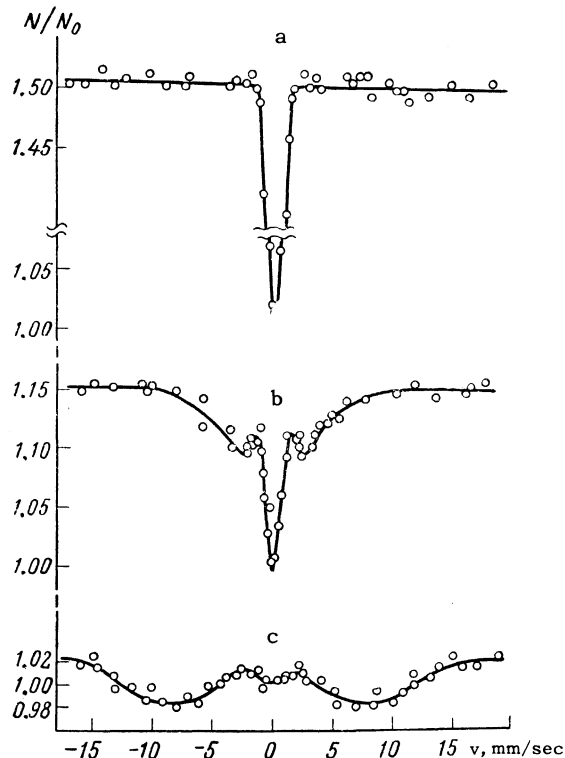


FIG. 3. Resonance absorption spectrum for sample containing 61.5%  $\text{BiFeO}_3$  at temperatures: a— $+160$ , b— $+23$ , c— $-196^\circ\text{C}$ .

measured at a temperature above the transition point. As for the shape and extent of the spectrum, one may say that such a picture could be gotten if the magnetic fields acting on the tin atoms in the sample had values up to 100,000 Oe (at room temperature); when the sample is cooled to liquid nitrogen temperature, the internal fields increase to 200,000 Oe.

The samples used in [3] were not sufficiently single-phase (according to the x-ray data), which caused a broadening of the region of the "jump," and left a sizeable value of the effect at temperatures below the "jump." In addition, this spoiled the temperature variation with composition and was the cause of the incorrect interpretation of the results.

Thus the "jump" in the value of the Mössbauer effect in solid solutions based on  $\text{BiFeO}_3$  is the result of magnetic hyperfine splitting (and not caused by a change in the probability of the effect,  $f'$ ), and is related to an antiferromagnetic phase transition. This conclusion is supported by the results of magnetic measurements.

<sup>1</sup> Fedulov, Venetsev, Zhdanov, Smazhevskii, and Rez, *Kristallografiya* 7, 77 (1962), *Soviet Phys. Crystallography* 7, 62 (1962).

<sup>2</sup> Kiselev, Ozerov, and Zhdanov, DAN 145, 1255 (1962), Soviet Phys. Doklady 7, 742 (1963).

<sup>3</sup> Pham Zuy Hien, Viskov, Venetsev, and Shpinel', JETP 44, 2182 (1963), Soviet Phys. JETP 17, 1465 (1963).

<sup>4</sup> Mitrofanov, Illarionova, and Shpinel', PTÉ,

No. 3, 49 (1963), Soviet Phys.—Instruments and Exp. Technique, No. 3, 415 (1963).

Translated by M. Hamermesh  
51

### STIMULATED EMISSION OF $\text{Nd}^{3+}$ IN $\text{CaF}_2$ AT ROOM TEMPERATURE

A. A. KAMINSKIĬ, L. S. KORNIENKO, L. V. MAKARENKO, A. M. PROKHOROV, and M. M. FURSIKOV

Institute for Nuclear Physics, Moscow State University

Submitted to JETP editor October 28, 1963

J. Exptl. Theoret. Phys. (U.S.S.R.) 46, 386-389 (January, 1964)

STIMULATED emission in crystals of the fluorite type ( $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$ ) containing  $\text{Nd}^{3+}$  at

room temperature has been observed so far only in the case of  $\text{SrF}_2$  [1]. The present communication gives preliminary results of an investigation of stimulated emission from  $\text{Nd}^{3+}$  in  $\text{CaF}_2$  at room temperature. The crystals used were grown from the melt in a fluorine atmosphere by slowly lowering the crucible; the crystals had various concentrations of neodymium oxide. Oscillation was observed in crystals with  $\text{Nd}_2\text{O}_3$  concentrations of 0.3 and 1.5% and occurred at a wavelength of about  $1.047 \mu$ . The electrical energy at threshold in the optical excitation system used was about 190 Joules for a crystal having an  $\text{Nd}_2\text{O}_3$  concentration of 0.3% (the crystal was 60 mm long and 6.5 mm in diameter).

Excitation of the system is by absorption of light

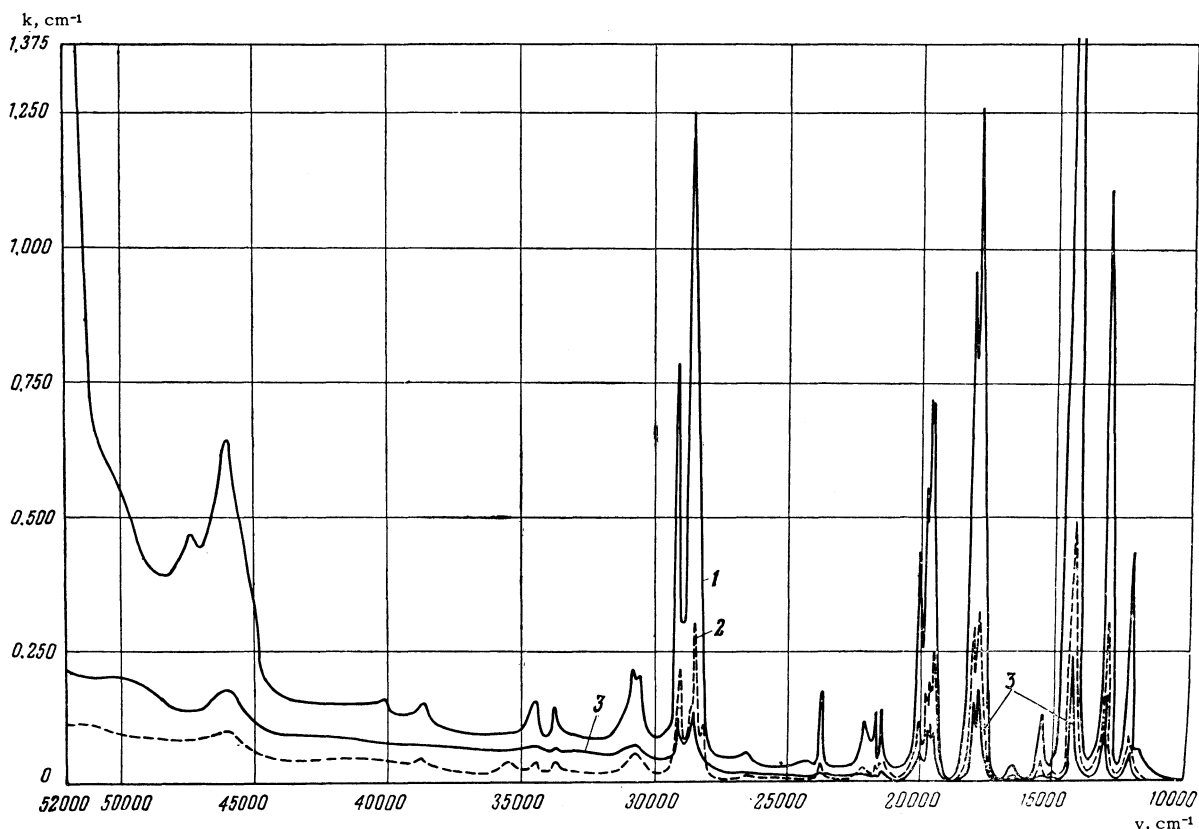


FIG. 1. Absorption spectra of  $\text{Nd}^{3+}$  in  $\text{CaF}_2$  at room temperature for various  $\text{Nd}_2\text{O}_3$  concentrations; 1—0.2%; 2—0.5%; 3—1.5%.