CONCERNING THE INTERACTION BETWEEN THE SPECIAL DIELECTRIC AND MAGNETIC PROPERTIES IN "FERROELECTRIC MAGNETS"

Yu. Ya. TOMASHPOL'SKIĬ, Yu. N. VENEVTSEV, and G. S. ZHDANOV

L. Ya. Karpov Physicochemical Institute

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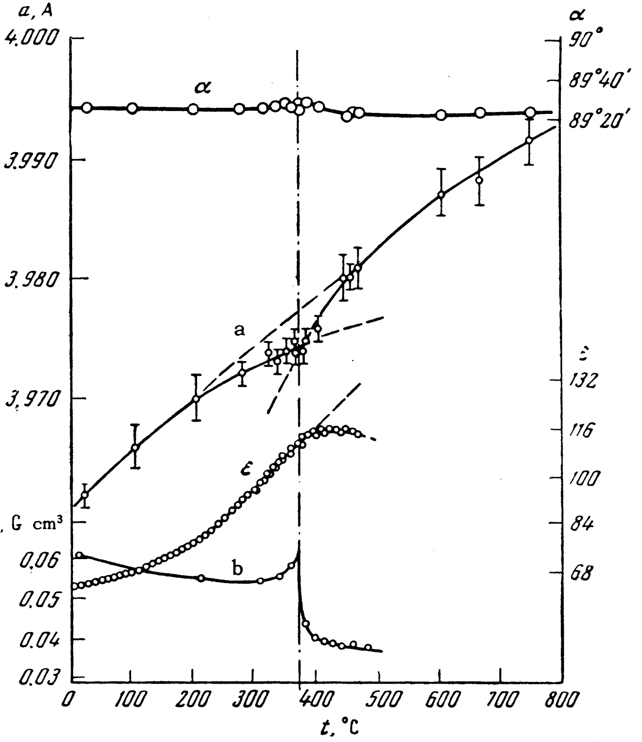
RECENTLY the idea of producing a new class of substances, which combine special dielectric and special magnetic properties, has come close to realization; we propose to call such substances "ferroelectric magnets." The investigation of these substances has been the subject of many theoretical [1,2] and experimental papers [3-5]. We can speak of electric and magnetic structures in "ferroelectric magnets" and on the connection between these dipole structures and the crystal atomic structure. In such compounds we should expect the manifestation of an internal connection between the electric and magnetic dipole structures.

In the present investigation an attempt was made to observe and study this connection in the "ferroelectric magnet" $BiFeO_3$, in which ferroelectric properties [6] as well as an antiferromagnetic structure [7] were observed in our laboratory, for the first time (the ferroelectric Curie point is $T_C = 850°C$ and the antiferromagnetic Neel point is $T_N = 370°C$).

Comprehensive investigations were made of the temperature dependences of the unit-cell parameters, the dielectric constant, and the specific magnetization, with special care taken in the region of the antiferromagnetic transition. In the presence of an interconnection between the electric, magnetic, and atomic structure, the antiferromagnetic transition at the Neel point should give rise to definite changes in the dielectric parameters and in the parameters of the crystal structure. If these changes are sufficiently large, they can be observed experimentally.

The x-ray diffraction measurements were carried out by us in filtered Cu radiation with a URS-50-IM diffractometer equipped with a high-temperature attachment designed for photography at temperatures up to 1,000—1,100°C (constructed in our institute) [8]. For the calculation we used the (420) reflection group at $\theta \sim 60°—62°$; the exact determination of the angles was carried out point-by-point, and the relative accuracy of most measurements was not lower than ± 0.001 Å for the period a, and not lower than ±3′ for the rhombohedral angle α. We have also attempted to investigate the temperature dependence of the dielectric constant of $BiFO_3$. To this end we used samples synthesized in an oxygen atmosphere at 780°C for 1.5 hours. This reduced the content of the Fe^{2+} ions, which play a noticeable role in the conductivity of the $BiFeO_3$. We were thus able to reduce the conductivity of the samples by 2—3 orders (to $10^{-8}—10^{-9}\ \Omega^{-1}\ cm^{-1}$).



Temperature dependences of the parameters of the atomic, magnetic, and electric structures for $BiFeO_3$: of the period a and the rhombohedral angle α of the unit cell, of the specific magnetization σ in a field H = 7800 Oe, and of the dielectric constant ϵ.

The measurements of $\epsilon(t)$ were carried out with standard apparatus at 200 kcs in a weak field, at temperatures from that of liquid nitrogen to $t \sim 500°C$. The magnetic measurements of the specific magnetization were carried out by the procedure described in [9]. The results of the experiments, shown in the figure, indicate that the cell parameter a has a general tendency to increase with the temperature, up to the attained temperature $t \sim 810°C$, above which the $BiFeO_3$ decomposes. The rhombohedral angle α does not change noticeably up to the decomposition, from which we can conclude that for $BiFeO_3$ T_C

lies above the decomposition point, in accordance with the earlier data [10]. The peculiarities of the a(t) and $\alpha(t)$ curves, as can be seen from the figure, are respectively the noticeable dip and the incipient jump in the region $t \sim 370°C$. The dielectric constant for $BiFeO_3$ increases monotonically with the temperature up to $t \sim 370°C$; in the 370—500° interval it remains approximately constant and even decreases somewhat on approaching $t \sim 500°C$, above which the measurements are made difficult by the sharp increase in the conductivity. The conductivity proper, as shown by the measurements, increases continuously with the temperature up to the attained $t \sim 650°C$. The samples obtained in the oxygen atmosphere have parameters $a = 3.962 \pm 0.001$ Å and $\alpha = 89°31' \pm 3'$, which coincide with the parameters of the samples obtained by annealing in air, while the peak on the curve of the specific magnetization (see the figure), as shown by magnetic measurements, is in the 370°C region, as in the case of $BiFeO_3$ samples obtained in the usual manner. At the same time, the samples obtained in oxygen display near room temperature a large spontaneous moment and some increase in the specific magnetization, which can be treated as a manifestation of weak ferromagnetism in the $BiFeO_3$ [11,9].

We believe that the noticeable anomalies in the curves of the cell parameter a, the angle α, and the dielectric constant ϵ in the region of the Neel point offer evidence of the existence of a connection between the magnetic, electric, and atomic structures. It is precisely by virtue of this connection that the sharp change in the magnetic structure at the point of antiferromagnetic transition leads to noticeable changes in the electric and atomic structures, as reflected in the anomalies of the corresponding parameters near the Neel point. Thus, the observation on our part of one of the manifestations of the aforementioned interaction in $BiFeO_3$ indicates that this connection is apparently detectable experimentally and can be observed and investigated in a comprehensive fashion, by studying the changes in the magnetic and electric characteristics and of the parameters of the atomic lattice as functions of several extraneous factors (temperature, pressure, fields, etc.). We note that in the case of external fields and unilateral pressures, the preferred orientation of the domains which results from this can leave a definite imprint on the investigated interaction picture. Thus, the connection can be regarded both on a unit-cell scale, as well as on a scale of multidomain formations in the case of single crystals or polycrystals.

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