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Low-frequency Magnetoelectric Resonances in $BaCoF_4$

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The frequency dependence of the transverse magnetoelectric effect in $BaCoF_4$ is investigated. It is shown that the observed resonances are not associated with acoustic oscillations of the sample, peculiarities of its electric properties or size effects. The strong influence of a weak pressure, which brings the magnetic layers of the substance closer together, suggests that the resonance properties observed at low frequencies are associated with the weak interaction between the layers.

A magnetoelectric effect in a $BaCoF_4$ single crystal has been reported in[1] and the magnetic properties of this substance have been investigated in[2]. In the present work we describe the sharp frequency dependence, observed here for the first time, that is exhibited by its magnetoelectric constants. It should be noted that this pronounced frequency dependence in no way follows from the familiar thermodynamic theory of the magnetoelectric effect.[3] A previous measurement[4] had shown that the magnetoelectric constant a_{11} for chromium oxide in the 200–20 000 Hz range is independent of the frequency within experimental error limits and that its value is practically in agreement with the results of static measurements.[5]

The results for $BaCoF_4$ in[1] were obtained with a conventional technique[6] using the technically most convenient frequency 10 kHz. An important property of $BaCoF_4$ is its very pronounced layered structure with an extremely weak interaction between the magnetic layers. It is well known that two-dimensional ordering is possible in such crystals.[7] The weak coupling of the magnetic layers and the large correlation radius for two-dimensional ordering lend credence to the hypothesis that resonant magnetic properties exist in the case of relatively low frequencies or anomalously long relaxation times.

We investigated the frequency dependence of the magnetoelectric constants using the technique described in[6] for the 10^3–10^5-Hz range. In contrast with the experimental work of[1], the static magnetic field was applied in a plane perpendicular to the axis of the measuring coils. The sizes and orientations of our $BaCoF_4$ single crystals permitted measurements only for an alternating electric field oriented parallel to the twofold axis. We determined the frequency dependence of the "alternating" magnetic moment $\widetilde{m}$ in the direction perpendicular to this axis. The frequency dependence of $\widetilde{m}$, registered with a narrow-band amplifier tuned to the generator frequency, reveals several sharp resonance peaks in the 4–15-kHz interval. No resonances were observed at lower frequencies. At higher frequencies the peaks become weaker and practically disappear above 20 kHz. The observed pattern depended sharply on the direction in which the "alternating" magnetic moment was measured and on the direction of the static magnetic field. The signal amplitude at the resonance peaks increases in proportion to the strength of the alternating electric field up to $\widetilde{E} \sim 3$ kV/cm and in proportion to the static magnetic field up to 6 kOe. Nonlinearity is observed at higher strengths of both fields. "Breaks" of the magnetization curves of $BaCoF_4$ appear at 6 kOe.[2] The frequency locations of the resonance peaks depend only on the crystal orientation with respect to the external fields $\widetilde{E}$ and H and on the direction in which the "alternating" magnetic moment is registered. We observed no shifting of the resonance peaks when the magnitude of $\widetilde{E}$ or H was changed at fixed orientations.

The observed resonance curves were not associated with the excitation of acoustic oscillations in piezoelectric $BaCoF_4$,[8] because for our samples the lowest possible resonance frequency of transverse oscillations, depending on the crystal size, was $\sim 3 \times 10^5$ Hz, whereas the observed resonances lie at least an order of magnitude lower. Also, an attempt to reduce the resonance amplitudes by various ways of cementing the crystal to the electrodes led to no change of the observed pattern as compared with the free crystal. It was also established that the investigated effect is not associated with the purely electric properties of $BaCoF_4$. The dielectric constant ϵ measured along the twofold axis in the same frequency interval does not vary to with ±0.1%. In these measurements we used strengths of $\widetilde{E}$ up to 0.5 kV/cm and magnetic fields to 20 kOe, at room temperature and at liquid nitrogen temperature. We also showed that the observed oscillations of magnetization are not associated with the resonance conditions for wave reflection from the sample boundary. To do this we recorded the frequency dependence for another $BaCoF_4$ single crystal three times larger than the first one. When both samples had the same orientation the resonance peaks of the second sample were shifted by at most a few per cent relative to the peaks of the first sample.

We can therefore assume that the observed resonance effects are associated with the properties of the substance itself. The linear increase of $\widetilde{m}$ with H in a very large range of field strengths suggests that the effect of the field does not consist in establishing a single domain in the crystal. The role of H consists most likely in the magnetizing of an oscillating structure. The observed linear dependence of $\widetilde{m}$ on H corresponds to terms of the form $P_iM_jM_k$ in the thermodynamic potential of the crystal as described in[9] for C_{2v} symmetry.

Figure 1 shows the frequency dependence of the "alternating magnetic moment along the a axis of the crystal (in the notation of[2]). It should be noted that when the direction of the external field is reversed the sign of $\tilde{m}$ relative to $\tilde{E}$ is reversed. Because of the complexity of the pattern we limited our work to measurements at the temperatures of liquid hydrogen and liquid nitrogen as well as room temperature. The strong linear growth of the signal amplitude as the static magnetic field is strengthened permits very large peak values of $\alpha = \tilde{m}/\tilde{E}$ up to 10^{-2}. We recall that α is of the order of 10^{-4} in Cr_2O_3.

We observe that with the reduction from room temperature to liquid nitrogen temperature all amplitudes increase by a multiple of a few times unity and that an additional sharp peak appears near 5 kHz. Further lowering of the temperature below the phase transition point at 65°K[2] leads to a small shift of this peak and to its splitting, while relatively weak and flat peaks are transformed as the frequency is increased into a sharp double peak near 8 kHz. At the same time the amplitudes of the magnetoelectric signals again increase strongly. The very high value of the magnetoelectric constant α at resonance makes it possible to observe the contribution of terms quadratic in P and M that exist in the thermodynamic potential for any magnetic structure but are customarily dropped when the coefficient is small (in[9], for example). The P^2M^2 quadratic terms should lead to a nonlinear dependence of $\tilde{m}$ on $\tilde{E}$ for large $\tilde{E}$ and to frequency doubling of the magnetoelectric resonance signal. The experimental results show that at the maximum values of $\tilde{E}$ small nonlinearity up to 4% actually appears. However, the frequency doubling effect became very prominent when the frequency of the external field $\tilde{E}$ equaled half the resonance peak frequency. In this situation the double-frequency signal (the frequency of the principal resonance) was several times stronger than the signal at the frequency of $\tilde{E}$. The amplitude of the double-frequency signal increased in proportion to $\tilde{E}^2$.

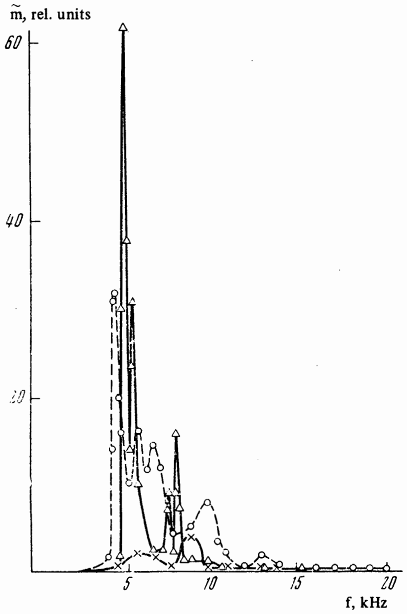

FIG. 1. Frequency dependence of the amplitude of the "alternating" magnetic moment at different temperatures: X–300°K, O–77°K, Δ–20°K; $\tilde{m}$ || a, H || $\tilde{E}$ || b.

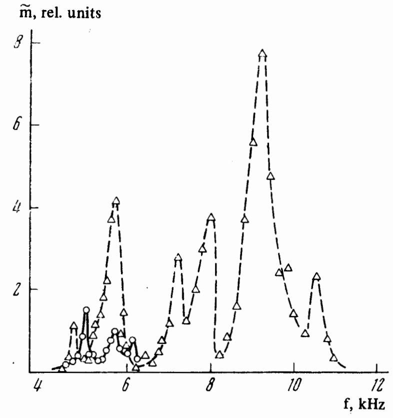

FIG. 2. Change in the frequency dependence of the "alternating" magnetic moment $\tilde{m}$ along the a axis of the crystal when pressure was applied along the b axis perpendicular to the magnetic layers. T = 77°K; O–σ = 0, Δ–σ = 200 kg/cm²; H || $\tilde{E}$ || b.

The most important fact to be considered in any attempt to interpret the observed frequency dependences consists in the extremely low resonance frequencies. For substances like $BaCoF_4$ it is most reasonable to assume that the investigated process is associated with the very weak interaction between different layers of the crystal. This hypothesis was confirmed by an experiment in which a pressure ~300 kg/cm² was applied perpendicular to the magnetic layers of the crystal by means of a simple screw mechanism. The frequency dependences were strongly influenced even by this low pressure. Figure 2 shows how the pressure affected a crystal having the same orientation as in Fig. 1. The deformation weakens and shifts the principal peaks, and a new group of peaks appears with higher amplitudes at higher frequencies. However, in the case of the frequency dependence of $\tilde{m}$ along the c axis the pressure shifted the entire pattern toward lower frequencies and enhanced the peak amplitudes (Fig. 3). The strong shifting of the frequency dependences when the magnetic layers move closer to each other indicates a relation between the observed resonances and the weak interaction between the magnetic layers. It can also be hypothesized that, in addition to the simple influence of deformation on the magnitude of the interaction between the layers, a transformation of the magnetic structure occurs under pressure. A

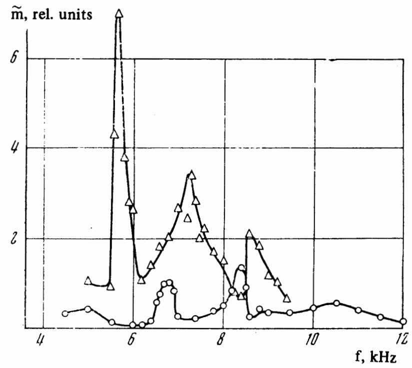

FIG. 3. Change in the frequency dependence of the "alternating" magnetic moment $\tilde{m}$ along the c axis of the crystal when pressure was applied along the b axis. T = 77°K; O–σ = 0, Δ–σ = 300 kg/cm²; H || $\tilde{E}$ || b.

similar situation was observed in samples of layered Rb_2MnF_4 and Rb_2MnCl_4.[10] However, the complexity of the pattern and the observed frequency shifts in different directions for different orientations prevent us from giving any detailed explanation of the observed effects.

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