Piezomagnetism of superconducting iron chalcogenides

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Experiments on the acoustoelectric transformation in superconducting compounds based on FeSe reveal the manifestation of piezomagnetism in them. It allows us to refer the family of superconducting chalcogenides to the systems with a hidden magnetic order and broken time-reversal symmetry. The anisotropy of the piezomagnetic response indicates that the crystal structure of these compounds belongs to the trigonal syngony, in the low-temperature phase.

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I. INTRODUCTION

This paper is devoted to the study of a mysterious, at first glance, effect which was found in Ref. [1], in the experiments on the acoustoelectric transformation (AET) in FeSe single crystals. In Ref. [1], an intense emission of a polarized electromagnetic wave was registered under high-frequency shear deformation of the sample, in the absence of the external magnetic field, below the structural transition temperature. Analysis of known mechanisms allowed to conclude that, most probably, the effect is accounted for the piezomagnetism, the phenomenon discovered in antiferromagnets more than half a century ago [2]. For the existence of such an effect, the thermodynamic potential should contain a term in the form of a product of the magnetic field and the deformation. But this term is not invariant with respect to the time reversal [3]. Piezomagnetism is not possible in crystals without the magnetic structure. At the same time, any long-range magnetic order was not observed in numerous studies of FeSe at normal pressure (see, e.g., Ref. [4]). For this reason, we think that the information on the existence of piezomagnetism in FeSe was not been accepted by the scientific community. Apparently, the prevailing opinion was that the observed AET response was due to accidental causes and was not of fundamental importance.

In this paper, in addition to pure FeSe samples, we investigated samples with partial substitution of selenium by sulfur (superconducting $FeSe_{1-x}S_x$ compositions). We found that all samples demonstrate the piezomagnetic effect of approximately the same intensity. Suitability of the ultrasonic technique for the study of the phenomenon of piezomagnetism was confirmed in our paper [5]: the estimated value of the piezomagnetic coefficient obtained by the AET experiment [5] on the reference piezomagnetic crystal CoF_2 practically coincided with the value known from the static measurements [2].

We also measured the magnetic susceptibility of the samples under investigation. No traces of magnetic inclusions were found. In addition, it was established that magnetic characteristics of the glued sample practically does not differ from that of the detached sample. It excludes possible side effects that, in principle, could be caused by magnetic impurities in the specific sample or by magnetic ordering induced by anisotropic thermoelastic stresses appearing during solidification of the acoustic grease.

The results obtained allow us to attribute the low-temperature phases of the family of superconducting $FeSe_{1-x}S_x$ ($x = 0$–0.14) to compounds with broken time-reversal symmetry and hidden magnetic order.

Basing on this interpretation, we conclude that the situation in chalcogenides is very similar to one in nonmagnetic HTSC cuprates in the pseudogap phase. Indeed, the discovery of the magneto-optical Kerr effect in HTSC cuprates [6] shows that the pseudogap phase is the state with broken time-reversal symmetry and with a hidden magnetic order. Peculiarities of the diffraction of polarized neutrons lead to the same conclusion [7]. A thorough study of the anisotropy of the nonlinear optical reflectivity of HTSC cuprates [8] allows one to conclude that the formation of the pseudogap phase follows the scenario of the type II phase transition, with breaking of the inversion and time-reversal symmetry, and with a simultaneous disappearance of the second-order axis.

A number of theoretical approaches give a recipe for constructing a phase with broken time-reversal symmetry, and, at the same time, nonmagnetic in the usual sense. The model of orbital currents assumes the existence of spontaneous currents of opposite chiralities in each crystallographic cell, which form intracell magnetic quadrupoles. Their condensation into the polar phase (with the translational invariance preserved) leads to the phase transition to the pseudogap state. A detailed analysis of various modifications of the model, satisfying the symmetry constrains and compatible with the existing experimental facts, is given in Ref. [9]. An inherently similar scenario [10,11] suggests the formation of a long-range order in a system of magnetoelectric quadrupoles associated with the copper ion. The mechanism of ordering is not discussed in detail in the cited papers, but we think that it should be a Jahn-Teller-type interaction with the lattice.

In Ref. [12], the ordering of magnetoelectric quadrupoles in iron chalcogenides in the low-temperature phase was considered. This ordering can be interpreted as a hidden long-range magnetic order. It is accompanied by a violation of time-reversal symmetry. In Ref. [12], possible neutron and x-ray diffraction experiments were proposed to confirm (or disprove) the hypotheses on such ordering. In this connection, we consider the observation of the piezomagnetic response in our experiments as a direct confirmation of breaking of time-reversal symmetry in $FeSe_{1-x}S_x$ ($x = 0$, 0.075, and 0.14) single crystals.

The "trajectory" of the transition to the state of hidden magnetism in iron chalcogenides may be more complicated than in cuprates. As follows from the results presented below, the piezomagnetic response emerges at the temperature T_s simultaneously with the ferroelastic structural transition [13]. As discussed in Refs. [9–11], all models of hidden magnetism that admit the linear Kerr effect are polar. It means that the initial parent state should allow the piezoelectric effect (see, for instance, Ref. [14]). But, according to the structural studies performed on powder samples [15], the crystal structure of the compounds discussed belongs to the centrosymmetric point group D_{4h}, at room temperature T_r. It means that a phase transformation to a state with broken inversion symmetry should occur between T_r and T_s. In the support of that, we draw the attention to the experiments [16,17], where it was reported on the features in the optical characteristics that indicate the possibility of FeSe transition to a pseudogap state. By analogy with cuprates, one can assume the lack of inversion symmetry in this state. We would emphasize that it is one of possible scenarios. In the general case, there is no need for such an assumption about the structural state of FeSe. Even-parity symmetry does not preclude the existence of piezomagnetism, and such configurations are possible in the loop current model [9]. The question of the polarity of the state can be solved in other symmetry-sensitive experiments.

II. EXPERIMENTAL TECHNIQUE

The technique of the experiment was practically the same as described previously [1,5]. All measurements were performed in the pulse mode. The shear deformation of a given polarization, generated by the piezoelectric transducer, is introduced into the sample through an acoustic delay line (DL). The electromagnetic field, arising in the sample under deformation, is radiated into the free space (in the first approximation, as a plane wave) and is registered by a frame antenna placed near (∼0.5 mm) the sample. The antenna can be rotated to measure the polarization diagrams. Recall that for a linearly polarized wave the maximum of the polarization diagram corresponds to the orientation of the electric and magnetic fields parallel and perpendicular to the plane of the frame, respectively. The DL provides the time separation of the electromagnetic signal emitted by the submillimeter-sized sample, and the parasitic signal caused by leakage of the exciting radio pulse. As a rule, a single crystal of undoped germanium oriented along the second-order axis was used as the DL. The DL of sufficient length (∼15 mm) allows one to work with elastic modes of given polarizations. Test measurements with the DLs made of leucosapphire and of molybdenum single crystals did not show any significant influence of the DL material on the effects observed.

We used the apparatus described in Ref. [18], which allows one to register simultaneously the amplitude and the phase of the electromagnetic signals at fixed frequency (∼55 MHz). The $FeSe_{1-x}S_x$ single crystals ($x = 0$, 0.075, and 0.14) grown by the technology described in [19] had a shape of thin (∼0.4 mm) plates with the cross-section dimension of 1–2 mm. The plane of the plates was orthogonal to the tetragonal axis with a good accuracy.

III. RESULTS AND DISCUSSION

In a nonmagnetic conducting medium, in the absence of an external magnetic field, and in the local limit ($ql \ll 1$, where q is the wave number, and l is the mean free path of charge carriers), only the Stewart-Tolman inertial field is the source of the AET response to a transverse sound wave [20]. In spite of a relatively weak intensity of the inertial field, this response was experimentally detected in borocarbides [21], and its characteristics were studied. In the single mode situation (i.e., when only one of two possible transverse modes is excited), the electric component of the radiated electromagnetic field is linearly polarized and oriented parallel to the displacement vector **u** in the acoustic wave. Deviations from the local limit result in deformation corrections, but the orientation of the electric field does not change. At $q\delta > 1$, where δ is the skin depth in the normal state, a characteristic feature of the AET response of the inertial nature is its rapid increase under lowering of temperature below the superconducting transition [21]. This increase is the result of the decrease of the London penetration depth.

In performing AET experiments with FeSe single crystals in the normal state, and in the absence of a magnetic field, contrary to the expectations, we observed an intense electromagnetic radiation with the vector **E** approximately orthogonal to **u**. The amplitude of the signal was almost of two orders of magnitude greater than the Stewart-Tolman component. It was also found that the AET response rapidly decreases in the superconducting phase. The analysis of experimental facts led us to the conclusion that piezomagnetism is the most appropriate mechanism to explain the observed phenomenon. At the same time, the lack of evidences for the existence of any magnetic order in FeSe was a serious obstacle in accepting such a point of view. It was suggested in Ref. [1] that magnetism in FeSe is of a fluctuation nature.

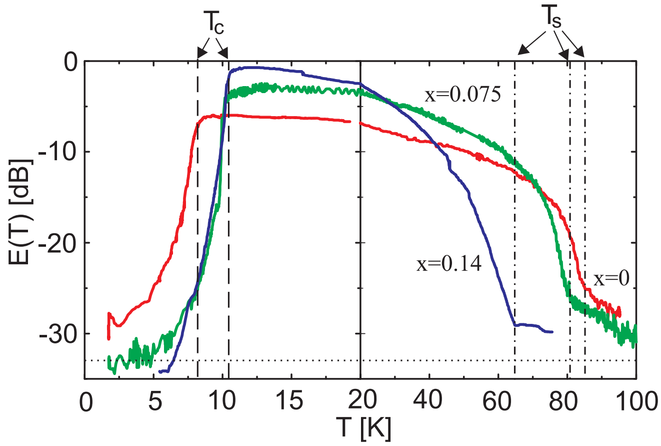

FIG. 1. The amplitude of the electromagnetic wave (the AET signal) radiated from the $FeSe_{1-x}S_x$ single crystals with different x subjected to the transverse elastic wave. The horizontal scale is stretched in the low temperature range. The dotted line shows the approximate level of detection of the signal against the background noise. The superconductive critical temperatures T_c and the temperatures of the structural transition T_s are shown by dashed and dash-dotted vertical lines, respectively.

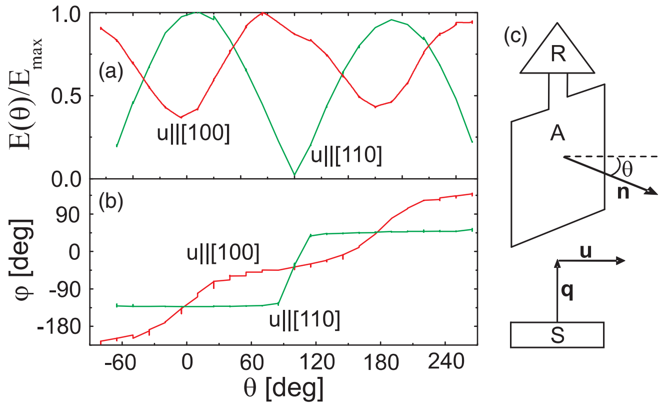

FIG. 2. Polarization diagrams of the $FeSe_{0.925}S_{0.075}$ sample at $T = 15$ K, $\mathbf{q}\|[001]$, $\mathbf{u}\|[100]$ (red lines), and $\mathbf{u}\|[110]$ (green lines). (a) The amplitude of the AET signal normalized to the maximum signal, (b) the phase of the signal, (c) schematic diagram of the experiment (S is the sample, the rectangular coil A is the antenna, **n** is the normal to the plane of the coil, R is the recording device, **q** is the wave vector, and θ is the angle between the displacement **u** in the acoustic wave and **n**).

However, the present understanding is that the intensity and noise characteristics of the effect observed are not consistent with the fluctuation hypothesis.

The synthesis of high-quality $FeSe_{1-x}S_x$ single crystals by D.A.C. [19] made it possible to extend similar AET experiments to them. It turned out that at least for $x \leqslant 0.14$ the phenomena interpreted as piezomagnetism are observed in the family of sulfur-substituted compositions. Figure 1 shows the electromagnetic response to the shear deformation for FeSe single crystals with different sulfur contents. In these experiments, the sound wave vector **q** was parallel to the tetragonal axis (in tetragonal reference frame). The polarization of the wave was not determined. The data shown in Fig. 1 were obtained by tuning the receiving antenna to the maximum signal. For all compositions we observed a sharp increase in the response in the vicinity of the temperature of the structural transition (T_s) of $FeSe_{1-x}S_x$. Weak temperature dependent AET signals were observed at $T > T_s$ as well. To make these weak signals visible, the data in Fig. 1 are presented in the semilogarithmic scale. The dotted line in Fig. 1 indicates the approximate threshold for confident detection of the AET response against the background noise.

In view of mechanisms of hidden magnetism discussed above, we imply that, in the system of magnetic or magnetoelectric quadrupoles, a long-range order is established due to their interaction with the deformation field arising from the structural rearrangement. At higher temperatures, the solidification of the acoustic grease (at 120 K) also probably causes orthorhombic distortions, leading to the appearance of a weak AET response. It is also possible that weak AET signals above T_s are caused by currents appearing due to emergence of transverse components of piezoelectric polarization.

The amplitude of the AET signal is determined by the structure of the polydomain phase varied from experiment to experiment, so the scale of changes in the AET response is varied markedly. Nevertheless, the qualitative similarity of the measured dependences in all samples without exception allows us to attribute the observed effect to the intrinsic property of the system, not related to the random characteristics of any particular sample.

A quick drop of the AET response at low temperature is caused by the rapid decrease of the penetration depth under the superconducting transition. We postpone the discussion on the mutual influence of piezomagnetism and superconductivity in iron chalcogenides to a separate paper. Here we just briefly touch this question in our argumentation.

The amplitude and phase polarization diagrams (rotation diagrams) were measured for different directions of the wave vector **q** and different directions of the displacement vectors **u**. The position of the antenna is characterized by the angle θ between the normal to the frame plane and the direction of **u** at the interface, where the sound wave is excited.

Figure 2 shows the results for $\mathbf{q}\|[001]$ (along the z axis) and two different orientations of **u**. Here and below the orientation of the displacement with respect to the crystal is given in the tetragonal reference frame, in view of possible formation of a polydomain structure below T_s. One can see qualitative differences between the rotation diagrams for two orientations of **u**. We interpret them as follows. Let us assume that we deal with an almost monodomain case. It is quite possible, since already at T_s, the sample is subjected to thermoelastic stresses generated in the plane, where the sample and the DL, oriented along the second-order axis, are glued together. In the low-temperature phase, the [110] direction is close to the second-order axis of the assumed orthorhombic phase, and, at $\mathbf{u}\|[110]$, one elastic eigenmode is presumably excited in the sample. The electromagnetic field radiated from the sample is linearly polarized. The polarization diagram is deeply modulated in the intensity, and the phase of the signal changes abruptly by π when the amplitude passes the minimum. Note that the magnetic component of the

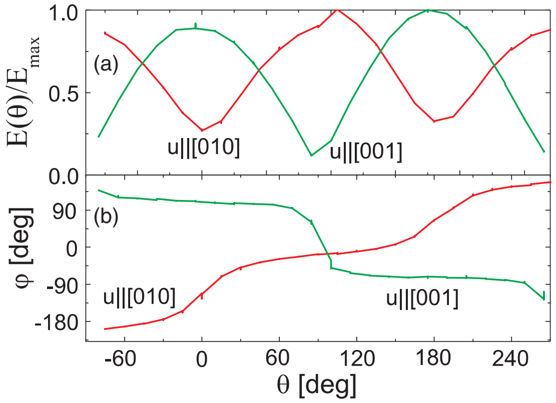

FIG. 3. Polarization diagrams of the $FeSe_{0.925}S_{0.075}$ sample at $T = 15$ K, **q**||[100], **u**||[010] (red lines), and **u**||[001] (green lines). (a) The amplitude of the AET signal, (b) the phase of the signal.

electromagnetic field is nearly collinear to the displacement in the elastic wave. At **u**||[100] in the low-temperature phase, two eigenmodes with mutually orthogonal displacements are excited. In the general case, these modes have different velocities. As a result, the output signal is elliptically polarized, the modulation of the amplitude diagram is significantly less, and the phase changes almost linearly with θ. In this case, the positions of the extremums in the intensity depend on the phase difference of two modes at the radiating interface. In particular, in Fig. 2, the maximum of the AET response for **u**||[100] is shifted almost by 90° to the maximum of the response at **u**||[110]. Since we assume that each mode generates the magnetic moment collinear to the displacement in the corresponding mode, the resulting phase shift between the moments should be close to π to realize such a displacement.

In a polydomain phase (which may appear as a result of structural transformation), we would observe the AET signal averaged over differently oriented domains in the acoustic beam zone. From the data presented in Fig. 2, we conclude about the predominance of domains of one orientation.

Similar features were observed at **q**||[100]. The results for two polarizations are shown in Fig. 3. One can see that at **u**||[001], the situation is close to the single-mode one, while at **u**||[010], it seems that we deal with the two mode case, also with the phase shift between the modes close to π.

Below we discuss the single-mode situation, which is simpler for the analysis. As follows from Figs. 2 and 3, in the single-mode situation the strain-induced component of the magnetic field is collinear to the displacement in the elastic wave, while the electric component is orthogonal to **u**. Using Maxwell's equations and the theory of elastic properties of metals [22], one can obtain the relation that describes the AET process in the harmonic approximation,

$$\nabla \times (\nabla \times \mathbf{E}) = -i\omega\mu_0(\mathbf{j} + \nabla \times \mathbf{M}), \tag{1}$$

where **E** is the Maxwell's field, **M** is the magnetization generated by the elastic deformation, μ_0 is the magnetic constant, and the current **j** is the sum of the electron current $\mathbf{j}_{\rm el}$ and the ion current $\mathbf{j}_{\rm ion}$. In the sound wave, these currents almost compensate each other. The uncompensated part is given by the Ohm law [22] $\mathbf{j} = \hat{\sigma}(\mathbf{E} + \mathbf{W})$, where $\hat{\sigma}$ is the conductivity tensor, and **W** is the extraneous field. The tangential component of the field **E** is continuous at the surface of the sample and it coincides with the electric field of the emitted wave.

In our case, in the absence of an external magnetic field, the extraneus field **W** includes the Stewart-Tolman field $\mathbf{u}_{ST} = m\ddot{\mathbf{u}}/e$ and the field $E_i \propto e_{ikl}u_{kl}$ caused by the piezoelectric effect (e_{ikl} is the piezoelectric tensor, and u_{kl} is the strain tensor). In principle, both components could lead to the appearance of $\mathbf{E}_\perp$ (the component of **E** orthogonal to **u**). In the plane wave, the derivative $d/d\mathbf{r}$ is replaced by $-i\mathbf{k}$, where **k** is a characteristic wave vector. Then, using Eq. (1), we obtain

$$\mathbf{E}_\perp = -\frac{k_0^2}{k^2 + k_0^2}\mathbf{W} - \frac{\omega\mu_0}{k^2 + k_0^2}(\mathbf{k} \times \mathbf{M})_\perp, \tag{2}$$

where $k_0^2 = i\mu_0\omega\sigma = 2i\delta^{-2}$, and δ is the skin depth. For simplicity, in Eq. (2), we imply that the conductivity is isotropic. In the superconducting state, the skin wave number k_0 in Eq. (2) is replaced by the inverse London penetration depth δ_L ($\delta_L^{-2} \gg |k_0^2|$). If the AET process is of a bulk nature, the only source of inhomogeneity is the sound mode, and the characteristic wave number k is equal to the sound wave number q. If, for some reasons, the AET is determined only by a surface process at the output interface, then $k \sim 1/a \gg 1/\delta_L$, where a is the lattice constant. In the latter case, the first term in the right-hand side of Eq. (2) would increase at the superconducting transition, and the second term would remain practically unchanged. But such a behavior contradicts the experiment Fig. 1, where the AET response decreases in the superconducting state. Therefore, an assumption on a possible surface nature of the discussed effects can be discarded. On the other hand, at $k = q$, the second term in the right-hand side of Eq. (2) decreases below T_c, because of the strong inequality $q\delta_L \ll 1$, which is satisfied at the frequencies used in the experiments.

The first term in the right-hand side of Eq. (2) describes the contribution of the Stewart-Tolman effect and possible contribution of the piezoelectic effect to the AET process. At $q\delta > 1$, this term increases at $T < T_c$. If only these mechanisms are responsible for the AET process, the AET response should grow rapidly in the superconducting phase. Just such a behavior was observed in borocarbides [21]. In the opposite limit ($q\delta \ll 1$), the first term in Eq. (2) remains practically unchanged at the superconducting transition. Thus, the assumption on the inertial or piezoelectric origin of the anomalous AET response in FeSe and $FeSe_{1-x}S_x$ contradicts the experiment, Fig. 1.

We note that Eq. (2) can be easily generalized to the case of anisotropic conductivity. In this case, the scalar quantities k_0^2 and $(q^2 + k_0^2)^{-1}$ should be replaced by tensors. The arguments on a minor role of the inertial or piezoelectric contribution remain valid. At the same time, due to the inequality $q^2 \gg |k_0^2|$ fulfilled in our experiments, such an anisotropy will not influence the contribution of the second term in Eq. (2) to the AET response.

In the general case, two mechanisms can provide the anomalous AET response: piezomagnetism and the anomalous Hall effect (AHE). For each of them the time-reversal symmetry should be broken, i.e., some axially ordered

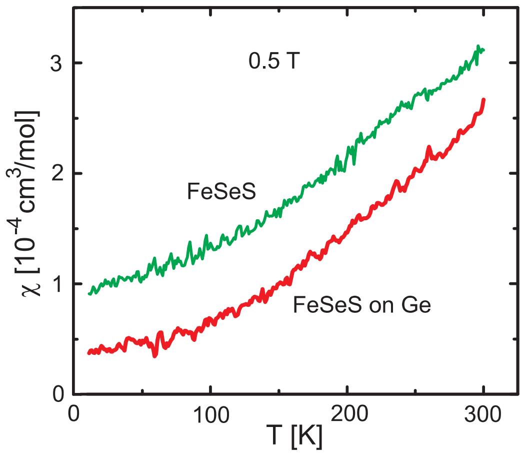

FIG. 4. Magnetic susceptibility of the detached $FeSe_{0.925}S_{0.075}$ single crystal (green curve) and the same crystal glued to Ge crystal (red curve) in the field $B = 0.5$ T. The germanium contribution is subtracted.

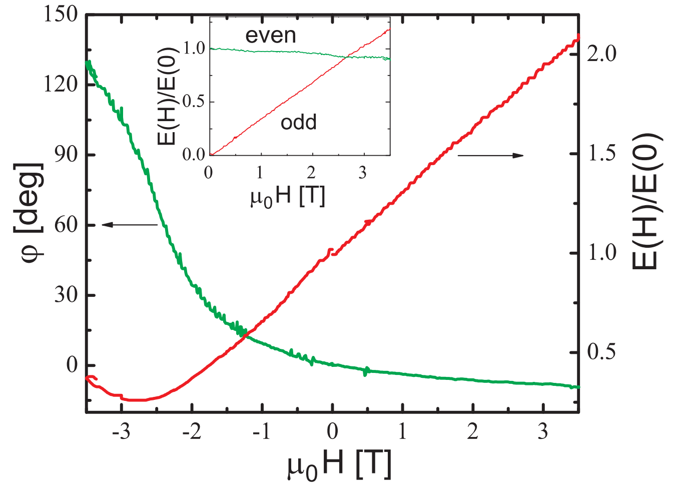

FIG. 5. Magnetic field dependence of the amplitude and the phase of the AET signal for the $FeSe_{0.925}S_{0.075}$ single crystal at $\mathbf{q}\|[001]$ and $\mathbf{u}\|[110]$. The amplitude and the phase are counted from their values at $H = 0$. The even and odd components of the amplitude of the AET signal are shown in the inset.

(magnetic) state is established in the sample. The piezomagnetic contribution to the AET is described by the second term in Eq. (2), and its behavior at $T < T_c$ is in a agreement with the experiment. Regarding to the specifics of the AHE in the superconducting phase, nothing is currently known about it. Below we will discuss the probable contribution of the AHE only with reference to the normal state.

In the literature, piezomagnetism and AHE are only considered with reference to systems with ferromagnetic or antiferromagnetic order. It is known that the antiferromagnetic phase is established in FeSe under uniform compression when the pressure exceeds some critical value ($P \sim 1$ GPa) [4]. One could suspect that, in our experiments, antiferromagnetic phase emerges due to thermoelastic stresses appearing during solidification of the acoustic grease (at $T \sim 110$–120 K). To exclude this possibility, the magnetic susceptibility of one of $FeSe_{1-x}S_x$ samples glued to Ge crystal with the same orientation and the same grease as in the acoustic experiment was measured (Fig. 4). The measurements were carried out by the MPMS-5XL Quantum Design SQUID magnetometer. One can see that, first, there are no traces of magnetic or paramagnetic inclusions, and, second, temperature changes in the magnetic susceptibility of the glued sample (with the contribution of Ge subtracted) practically do not differs from ones of the detached sample. No appreciable features are observed at the temperature of solidification of the grease and at the temperature of the structural transition. A small diamagnetic shift of the glued sample with respect to the detached sample is apparently related to the contribution of the acoustic grease. Thus we excluded side effects caused by possible presence of magnetic inclusions in the sample and by thermoelastic stresses appearing during solidification of the grease. It allows us to relate the effect observed with hidden magnetic ordering. In this case, piezomagnetism and AHE are quite admissible from the phenomenology, although a microscopic analysis of these effects for this type of magnetic ordering is currently absent.

In the external magnetic field $\mathbf{B}\|\mathbf{q}$, the Hall component, $\dot{\mathbf{u}} \times \mathbf{B}$, is added to the extraneous field in the expression for the current $\mathbf{j}$. Then the component of the electric field orthogonal to $\mathbf{u}$ and odd with respect to $\mathbf{H}$ arises. It interferes with the even in $\mathbf{H}$ signal discussed above. At certain magnitude and direction of $\mathbf{H}$ the amplitude of the resulting signal passes through the minimum and its phase changes by the value close to π. An example of such a dependence is shown in Fig. 5. Note that the complete compensation of the signals does not occur due to a residual ellipticity, although at more careful adjustment, it is possible to achieve almost complete compensation [1].

A simple procedure of decomposition of the resulting signal into the even and the odd components (Fig. 5, inset) allows one to determine the field H_0 at which the contribution of the piezomagnetic and/or the AHE compensates the contribution of the conventional Hall effect. The decomposition is performed according to the standard scheme,

$$E(H, \varphi)_{\pm} = \frac{E[+H, \varphi(+H)] \pm E[-H, \varphi(-H)]}{2}, \quad (3)$$

where the electric fields are considered as a complex valued quantity, with the module and the phase counted from the reference values in zero magnetic field. The upper (lower) sign refers to the even (odd) in H component. The result is shown in the inset of Fig. 5, from which it follows that the amplitudes of the even and odd components are aligned at $B_0 = \mu_0 H_0 \approx 3$ T. Knowledge of B_0 allows to estimate the parameters which determine the effect considered (see below).

Basing on phenomenological reasons, we imply that the total current in Eq. (1) contains the anomalous component $\mathbf{j}_{an}$. For magnetically ordered media, the current $\mathbf{j}_{an}$ represents the fraction of the transport current caused by the spin-dependent scattering of charge carriers on the magnetic structure. This current is orthogonal to the transport current. The current $\mathbf{j}_{an}$ is proportional to some axial vector which describes the magnetic order, and the AHE is connected with this current. It is currently unknown whether the hidden magnetic order leads to a similar phenomenon. However, since some axial vector that describes the hidden order should exist, one can assume the appearance of $\mathbf{j}_{an}$. In the sound wave, the transport current should be understood as the electron component of the total current, and $\mathbf{j}_{an}$ can be defined as $j_{an} = \beta j_{el} = -i\omega\beta neu$, where β is the "branching" ratio.

In the external magnetic field $\mathbf{B}\|\mathbf{z}$, the transverse sound mode with $\mathbf{u}\|\mathbf{x}$ produces the y-component of the field $\mathbf{E}_\perp$, which satisfies the equation

$$\left(q^2 + k_0^2\right)E_y = -k_0^2\left(i\omega uB - \frac{i\omega\beta m}{e\tau}u\right) - \omega\mu_0 qM_x, \quad (4)$$

where τ is the relaxation time.

For the further discussion it is instructive to evaluate the order of magnitude of the parameters in Eq. (4). For the speed of the transverse sound $s \approx 1.4 \times 10^5$ cm/s [13], we obtain the wave number $q \approx 2.5 \times 10^3$ cm^{-1}. The resistivity data ($\rho \sim 50\ \mu\Omega$ cm [23]) give $|k_0^2| \sim 10^5$ cm^{-2} and $\tau \sim 10^{-12}$–10^{-13} s at the density of carriers $n \sim 10^{20}$–10^{21} cm^{-3} [24].

It is of interest to estimate the maximum amplitude of the displacement u_{max} in our experiment. We use the piezoelectric transducers (resonating at the fundamental frequency) made of rotated y-cut lithium niobate, with the angle between the normal to the cut and the z axis, $\Theta = 108^\circ$ [25]. To provide the mechanical stability, the transducers are glued to the massive brass electrode. Direct measurement of the maximum amplitude of the high-frequency potential gives $V_{max} \approx 300$ V in the pulse. It allows us to calculate the peak density of the electric energy in the piezoelectric transducer of a given thickness (for the known dielectric constant of the transducer). Then, implying the electromechanical coupling coefficient $k_{coupl} \sim 0.7$ [25], we estimate the peak density of the elastic energy. Assuming that the losses in the grease are negligible, taking into account the acoustic impedances of Ge and FeSe, and the doubling of the amplitude at the radiating interface, we obtain $u_{max} \approx 80$ Å. Despite a rather large u_{max}, all measurements in the normal phase correspond to the linear regime.

Let us first assume that the observed phenomena are due to the AHE. Taking into account that at $B_0 \approx 3$ T, the responses due to AHE and the normal Hall effect should be equal to each other, we obtain the estimate for the branching ratio $\beta = \Omega_0\tau = 0.05 - 0.5$, where $\Omega_0 = eB_0/m \approx 5 \times 10^{11}$ s^{-1} is the cyclotron frequency. However, even in strong ferromagnets, the value of β does not exceed 10^{-2} [26]. Thus the assumption on the predominant AHE nature to the discussed phenomena is unlikely. Nevertheless, let us estimate the maximum hypothetical amplitude of the magnetic field generated by shear deformation in the AHE regime. In the emitted wave, the electric and magnetic components are mutually orthogonal, and their modules are equal to each other in Gaussian units. In the absence of the last term in Eq. (4), the field $\mathbf{B}$ is continuous at the interface, and we obtain

$$B_x = \frac{E_y}{c} = \left|\frac{k_0^2}{k_0^2 + q^2}\right|\frac{\omega}{c}u_{max}B_0 \approx 4 \times 10^{-10}\ \mathrm{T}. \quad (5)$$

In deriving Eq. (5), we take into account that two terms in the round brackets in Eq. (4) should compensate each other at $B = B_0$ and $M_x = 0$. On the other hand, implying the purely piezomagnetic origin of the AET signal ($\beta = 0$), from the conditions of the mutual compensation of the contributions

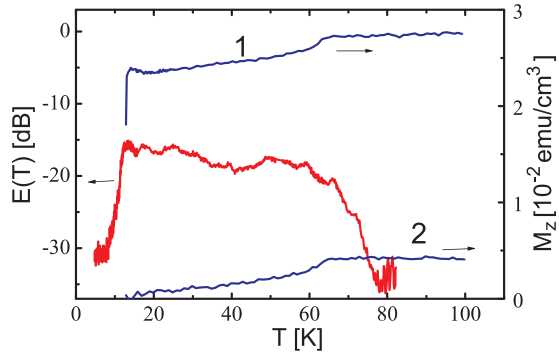

FIG. 6. Temperature dependence of the AET response of the $FeSe_{0.5}Te_{0.5}$ single crystal, and temperature dependence of its magnetization in the field $B = 0.02$ T (curve 1) and $B = 5 \times 10^{-4}$ T (curve 2).

of the normal Hall effect and the internal magnetization at $B = B_0$, from Eq. (4), we obtain

$$B_x = \mu_0 M_x = \frac{|k_0^2|}{q}u_{max}B_0 \approx 10^{-4}\ \mathrm{T}. \quad (6)$$

The behavior of the AET response in the superconducting phase allows us to conclude that the magnetic field, induced by the deformation, is comparable in magnitude to the lower critical magnetic field. But the latter is much larger than B_x given by Eq. (5). Therefore the AHE cannot be considered as the main source of the AET signal. Thus the most probable mechanism for the AET response observed is piezomagnetism.

The results presented in Fig. 2 imply that the thermodynamic potential contains the terms $H_x u_{xz}$ and $H_y u_{yz}$, where u_{ik} is the deformation tensor (here the axes notations correspond to the assumed orthorhombic syngony), but since all terms should be invariant under any symmetry transformation of a given crystal, the x and y directions cannot be the second-order axes. In other words, the phase formed as a result of the structural transformation cannot belong to the orthorhombic syngony. Similarly, the data in Fig. 3 imply the presence of the terms $H_z u_{xz}$ and $H_z u_{yz}$. It forbids the z direction be the second-order axis as well. This consideration forces us to classify the structural transition in the studied chalcogenides as not a tetraortho transition. The only possible variant is the structural transition into the triclinic phase. This conclusion correlates with the results of the first publication [27] devoted to FeSe superconductors, where it was reported that the phase formed under the structural transformation belongs to the triclinic syngony.

In Fig. 6, we present the results of the measurements of the AET response in the $FeSe_{0.5}Te_{0.5}$ single crystal. The sample was synthesized in Institute of Solid State Physics, Bulgarian Academy of Sciences by means of the self-flux technique. The procedure of fabrication of $FeSe_{0.5}Te_{0.5}$ single crystals is described in Ref. [28]. The data shown in Fig. 6 were obtained under propagation of the transverse sound along the z axis. We do not determine the orientation of the displacement $\mathbf{u}$ in the basal plane with respect to the crystallographic axes. For the comparison with the results for the $FeSe_{1-x}S_x$ system, the data presented in Fig. 6 are related to the maximum of the AET signal in Fig. 1. One can see that, qualitatively, the behavior of the AET response in $FeSe_{0.5}Te_{0.5}$ resemble the results shown in Fig. 1, although the value of the signal is approximately one order of magnitude smaller. The mechanism of the rapid growth of the response in the range 60–75 K is not clear. According to the review [29], no structural transition was observed in this compound, although Ref. [30] states that the low-temperature phase of this compound belongs to the orthorhombic syngony.

In Fig. 6, the results of measuring of the z component of magnetization in the field $B = 0.02$ T (curve 1), and in the residual field of a solenoid $B \approx 5 \times 10^{-4}$ T (curve 2) are also shown. From these results one can conclude that the sample studied has a residual z component of magnetization of the order of 10^{-2} emu/cm^3 which exists up to room temperature (not shown in Fig. 6), and reduces below 65 K until it vanishes completely near T_c. Perhaps, this behavior and the AET transformation behavior are correlated.

More detailed magnetic measurements [28] of the $FeSe_{0.5}Te_{0.5}$ crystal obtained by the same technology revealed the presence of a background magnetism in it at $T < 120$ K. It is presumably caused by nanocluster ferrimagnetic inclusions of Fe_7Se_8 at the level of $\sim$5%. In this connection, one could think that these inclusions are responsible for the piezomagnetic response we observed. However, a decrease of the AET response at the superconducting transition, similar to one presented in Fig. 1, is possible only under a very special distribution of these inclusions, namely, they should be located near the emitting surface within the skin depth of the normal phase, but they should not be present just at this surface. There is no reason to expect such a distribution of inclusions. Most likely, in this case, piezomagnetism comes into play as well. Study of samples free (or almost free) of magnetic inclusions may finally clarify this question.

IV. CONCLUSION

In conclusion, the acoustoelectric transformation in superconducting compositions of the iron chalcogenide family $FeSe_{1-x}S_x$ ($x = 0,\ 0.075,$ and 0.14) was studied. In all samples, regardless of the composition, the shear ultrasonic mode excites a linearly polarized electromagnetic field in which the magnetic component is collinear to the elastic displacement.

According to Maxwell's equations, it is possible only if the acoustic deformation excites oscillations of the electric current orthogonal to the direction of ion displacements in the sound wave. In principle, such oscillations would be excited without involvement of magnetic interactions. In this case, one should expect an increase in the acoustoelectric response due to a decrease in the superconducting penetration depth. However, since in superconducting state the amplitude of the emitted field decreases rapidly, this scenario is ruled out. Another possible scenario (piezomagnetic) is associated with the appearance of oscillations of the magnetic moment, collinear to the vector of ion displacements in the sound wave. The piezomagnetic hypothesis is completely consistent with the AET behavior in the supercondicting state.

The acceptance of the piezomagnetic hypothesis leads to two conclusions. Fist, all considered compositions belong to the systems with broken time reversal symmetry, i.e., being in a magnetically ordered state. In the absence of external perturbations, the spins and orbital moments are oriented in such a way that the resulting magnetic moment is zero in each unit cell. Due to the interaction, presumably through the lattice, a long-range order is established in the system at the temperature of the structural transformation, i.e. elementary moments are oriented uniformly in each cell of any individual domain. External deformations lead to a partial uncompensation of magnetic moments in each domain, turning the sample into a weak ferromagnets. It is the main conclusion of this paper. Second, the effect is observed under propagation of the sound wave along all major crystallographic directions. Symmetry consideration leads to the conclusion that the low temperature phase (below the structural transition) belongs to the triclinic syngony.

The proposed interpretation of the experimental results presented attributes chalcogenides (along with cuprates) to the compounds in which a new type of magnetic ordering, hidden magnetism, is realized.

A significant feature of experimental results presented is a rather sharp increase of the AET response under structural transition. We believe that this transition causes a generation of long-range elastic fields, that leads to the establishment of the long-range order in the system of magnetic or magnetoelectric quadrupoles. However, the structural transformation is usually accompanied by the formation of a domain structure. One would think that the observed effects are connected with motion of domain walls in the field of the ultrasonic wave. In Ref. [31], we present recent results of AET experiments on $FeSe_{0.82}S_{0.18}$ single crystal that exclude such an interpretation. This compound do not undergo structural transformations in the free state. It remains in the tetragonal phase up to the superconducting transition temperature [32]. Nevertheless, we observed the AET response of somewhat lower intensity which can be interpreted as piezomagnetism. Apparently, in this case, the long-range magnetic order is connected with the thermoelastic stresses that emerge in our experiments. It is possible that the same mechanism of ordering is realized in $FeSe_{0.5}Te_{0.5}$.

And finally, the key point of the proposed interpretation is the complete compensation of dipole magnetic moments in each unit cell. It is unclear now, at what stage it happens, either at the synthesis stage or at some intermediate temperature.

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