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Flexoelectric effect in GeTe

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Received November 21, 2024
Revised November 24, 2024
Accepted November 28, 2024

Germanium telluride (GeTe), being chemically and structurally very simple, possesses a plethora of functional properties. It is a semiconductor that becomes a superconductor under pressure, a high-temperature ferroelectric, a model phase-change material, a good thermoelectric and the material with a giant Rashba effect. In this work, by means of first-principle simulations and electrical measurements we demonstrate that thin slabs of GeTe may be flexoelectrics. In combination with the Rashba effect these findings suggest a new — mechanical — way to control the materials spin properties paving way to creation of novel spintronic devices.

Keywords: Germaniun telluride, ferroelectic, first-principle simulations, flexoelectric effect, spintronics.

DOI: 10.61011/PSS.2024.12.60218.317

1. Introduction

Material science is one of the most intensively developing fields of science and engineering, and special attention is paid to studies of multifunctional materials. At first sight a material must have complex composition and structure to ensure multifunctionality. Binary germanium telluride (GeTe) convincingly rebuts this paradigm, being a unique material, which, despite a quite simple composition, has a wide range of properties that are attractive for practical use, many of which found application in instrument structures and various devices.

Firstly, GeTe is a semiconductor, which becomes a superconductor under pressure [1]. Secondly, it is a high-temperature ferroelectric with Curie temperature $T_c = 630-670$ K, which has only two atoms in a primitive cell [2–9]. Thirdly, it is an efficient thermoelectric [10–14]. Fourthly, it is a so called phase-change material, which may quickly and stably switch between crystalline and amorphous states when exposed to short current or light pulses [15]. Thermoelectric properties of GeTe and its phase-change capability are widely used in thermoelectric converters, devices of optical and nonvolatile electronic memory, and in reconfigurable photonics. Several years ago it was shown that GeTe has a record-high Rashba effect [16–19], which opens the opportunities for its use in spintronics. Besides, both volume and surface Rashba effect is identified in GeTe films [20,21].

Many multi-component compositions may „envy“ such abundance of useful functional properties in such a seemingly simple material [22,23]. In this paper we demonstrate that germanium telluride has another functional quality: this material also has a pronounced flexoelectric effect (polarization response to deformation gradient) [24–32]. Such „new“ capability of polarization control is of great applied value, expanding the capabilities of GeTe use in a range of practically important ferroelectrics, ferroelectrics-multiferroics, ferroelectrics-superconductors, related polar materials in various instruments and devices of current electronics, optics and spintronics [33–37].

Contrary to most ferroelectrics, where the direction of dipole moment may be controlled using the external magnetic field, in GeTe such method of polarization control is complicated due to high electroconductivity of the materia, even though the possibility of dipole moment rotation in thin epitaxial GeTe films was demonstrated using force microscopy of piezoelectric response [38]. Therefore, a question arises on the alternative methods of action at thin GeTe plates, which may cause the dipole moment rotation.

Covalent radii of tellurium (1.36 Å) and germanium (1.21 Å) differ greatly, therefore one would remember Gorsky effect [39], predicted already in 1935. The essence of this effect is that under heterogeneous deformation of the crystal, for example, bending, atoms (ions) of material are exposed to forces that depend on atom dimensions, so that atoms with large radius move to the crystal field of tension, and atoms with smaller radius — to the field of compression, besides, this effect is reversible. It is logical to suggest that in case of polar links such atom displacements may cause formation of dipole moment (induced polarization) in the initially centrosymmetric crystal due to flexoelectric effect, which is a polarization response to deformation gradient.

The objective of this paper is inspection of this hypothesis (existence of flexoelectric effect in GeTe) and its complex investigation by performance of *ab initio* calculations of polarization and optical properties of bent and non-deformed GeTe plates and completion of electrical measurements.

2. Calculation method and experimental technique

Researching the theoretically flexoelectric effect in thin GeTe plates by performance of *ab initio* calculations of polarization response to deformation gradient, we face the task of calculating the inducted macroscopic polarization [40].

Ab initio polarization calculations were performed by us with Berry phase method [41–47], implemented in the plane-wave code CASTEP [48,49]. The calculations were made with generalized gradient exchange-correlation functional in the form of PBEsol [50] and two types of scalar-relativistic pseudopotentials, which describe the interaction of valence electrons with ion cores. The calculations of spontaneous polarization of volume rhombohedral phase of GeTe and $LiTaO_3$ used optimized norm-conserving Vanderbilt pseudopotenials proposed by Hamann in paper [51], which provide for high accuracy of calculation and were taken from Schlipf–Gigi database (released on 2020-02-06) [52]. The calculations of induced polarization of quasi-two-dimensional model GeTe plates used so called ultrasoft pseudopotentials from the base of CASTEP code itself, generated with gradient exchange-correlation functional in the form of PBE [53]. Additionally much more demanding calculations were made with ONCV pseudopotentials, the numerical results of which are provided in the paper.

Experimental verification of the obtained results was carried out on thin-film GeTe specimens. The specimens were planar structures with tungsten electrode, between which a GeTe layer with thickness of 130 nm was applied by magnetron sputtering method. The substrate used was flexible polyimide (kapton). After sputtering, the film was annealed at temperature of 250°C, and crystallized into rhombohedral structure with spatial group $R3m$, which was confirmed by X-ray diffraction analysis.

The specimen was attached fixedly on a special form. Using tungsten probes, the specimen edges were punched for bending, and electric connection was also provided to power supply source Agilent E3647A and to picoamperemeter Keithley 6485. The specimen resistance was measured at various bending degrees. Since the zonal structure of semiconductor (i. e. its resistance) varies as it is deformed, which is at the heart of straintronics, changes in resistance under bending may serve as indirect confirmation of the flexoelectric effect presence.

3. Results and discussion

Low-temperature (ferroelectric) GeTe phase, which is stable up to temperatures of around 630–670 K [3,8,9], is rhombohedral, and may be conventionally presented as a distorted lattice of table salt type, where atoms of one sort are somewhat moved from centrosymmetric positions, so that sublattices of short (2.82 Å) and long (3.15 Å) links of Ge–Te are formed. Besides, valence angles are somewhat distorted, so that the lattice stops being cubic. The structure of rhombohedral germanium telluride (with spatial group $R3m$) is shown in Figure 1, *a*. Shorter (stronger) links are shown with thicker two-color cylinders, longer (weaker) links are not shown. The presence of alternating short and long links of Ge–Te in the structure causes appearance of dipole moment in the material (spontaneous polarization). Note that as temperature increases, the distribution of long and short links becomes stochastic, and material becomes a paraelectric [54]).

Let us go back to review of a thin GeTe plate made of odd number of atom planes and limited at both sides, for example, by atom planes of tellurium. Such structure is symmetric, and after relaxation by density functional

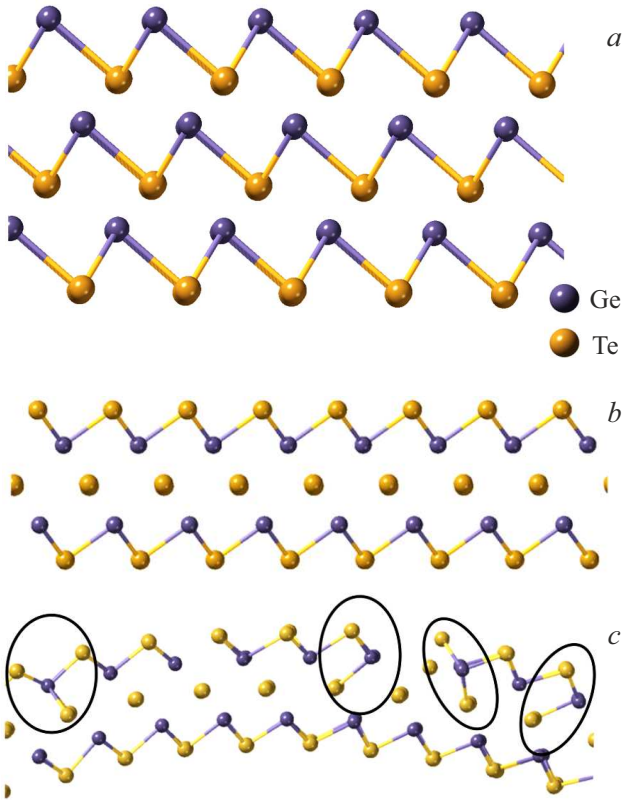

Figure 1. (*a*) Structure of rhombohedral GeTe phase. Short links (< 2.9 A) are shown with two-color cylinders, long (~ 3.3 A) links are not shown. Relaxed structure of straight (*b*) and bent (*c*) five-layer piece of Te–Ge–Te–Ge–Te. The short links are shown with two-color cylinders. One can see that in the nondeformed five-layer piece the dipoles in the upper and lower regions fully compensate each other, while in the bent structure the Ge–Te dipoles are maintained only in the lower region. In the upper region, structural units Te–Ge–Te are partially formed, which do not have a dipole moment, as a result of which the total dipole moment of the plate becomes different from zero.

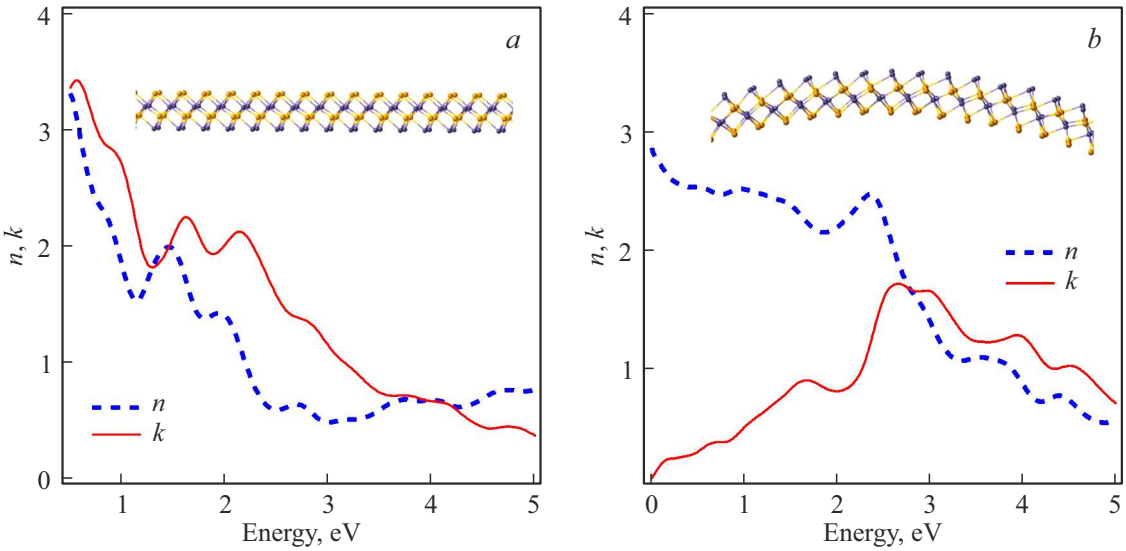

Figure 2. Optic constants of straight (a) and bent (b) plate Ge−Te−Ge−Te.

method looks like shown in Figure 1, *b*. Here solid two-color lines show pairs of Ge−Te, located at a distance of < 3 Å from each other. Longer Ge−Te links are not shown as before. One can see that in this structure two layers are formed (upper and lower), with opposite electric dipoles formed by difference of electronegativities of two elements so that the total dipole moment (polarization) of the plate is equal to zero.

Figure 1, *c* shows the structure of such plate bent with curvature radius 130 Å. One can see that while dipoles are maintained in the lower layer, some Ge atoms of the upper layer start interacting with the initially central layer of tellurium atoms, which is initially located at a larger distance, so that resonant links form non-polar Te−Ge−Te fragments so that the total dipole moment of the upper layer decreases, and that means that the resulting dipole moment of the plate becomes different from zero. Qualitative discussions above are confirmed by the results of polarization calculations.

While the dipole moment (spontaneous polarization) of the nondeformed GeTe plate is equal to zero, after bending the inducted polarization appears equal to $\sim 1.0\,\mu$C/cm^2. Is it high or low? For comparison, we calculated the spontaneous polarization of thin GeTe plate in rhombohedral phase made of four atom planes Ge−Te−Ge−Te. The calculated polarization of such plate was $\sim 0.9\,\mu$C/cm^2. In other words, the value of flexoelectric polarization occuring under bending of symmetric plate Te−Ge−Te−Ge−Te, turns out to be of the same order as the calculated spontaneous polarization of the plate (Ge−Te−Ge−Te) of rhombohedral GeTe with the same thickness.

As a result of the above noted pronounced conductivity, the correct experimental definition of dielectric polarization (difference of polarizations) of GeTe using standard methods of dielectric hysteresis loop (hysteresis loop-method) or pulse field measurement (pulsed-field method) is complicated. The calculations help to bypass this problem. The ab initio calculation of spontaneous polarization in the volume rhombohedral GeTe phase provided the value of $49\,\mu$C/cm^2. This value is comparable to experimental values of spontaneous polarization of such ferroelectric materials as $BaTiO_3$ ($26\,\mu$C/cm^2), $KNbO_3$ ($30\,\mu$C/cm^2), $LiNbO_3$ ($71\,\mu$C/cm^2), $LiTaO_3$ ($50\,\mu$C/cm^2) [45]. The experimental value of spontaneous polarization for volume rhombohedral GeTe phase is not known to us, therefore, to verify its theoretical value obtained in this paper, in the same approximations we calculated the spontaneous polarization of crystal $LiTaO_3$, for which value $46\,\mu$C/cm^2 was obtained, being well-matched with the experimental value $50\,\mu$C/cm^2.

In addition to the ab initio calculations of induced polarization in GeTe bent plates, the results of which directly indicate a flexoelectric effect, we also made calculations of optical constants. It turned out that refraction and extinction indices of bent plates calculated by us „ab initio“ differ significantly from such for nondeformed plates (Figure 2), which means a sharp contrast of their optical properties specific for phase-change materials. In our opinion, this may also be treated as an additional evidence of flexoelectric effect presence.

For experimental verification of flexoelectric effect, thin GeTe (~ 130 nm) film was formed by magnetron sputtering. The film was bent, and electrical resistance of the film was measured at the same time. The result given in Figure 3 shows that the resistance of the film reversibly changes when bent, and in the bending interval of 20−50 degrees the resistance value under load is higher than without one.

Despite the fact that the direct analysis of the result within the flexoelectric effect is complicated by the fact that the crystallized film is polycrystalline, the experiment unambiguously demonstrates that the bending of GeTe layer

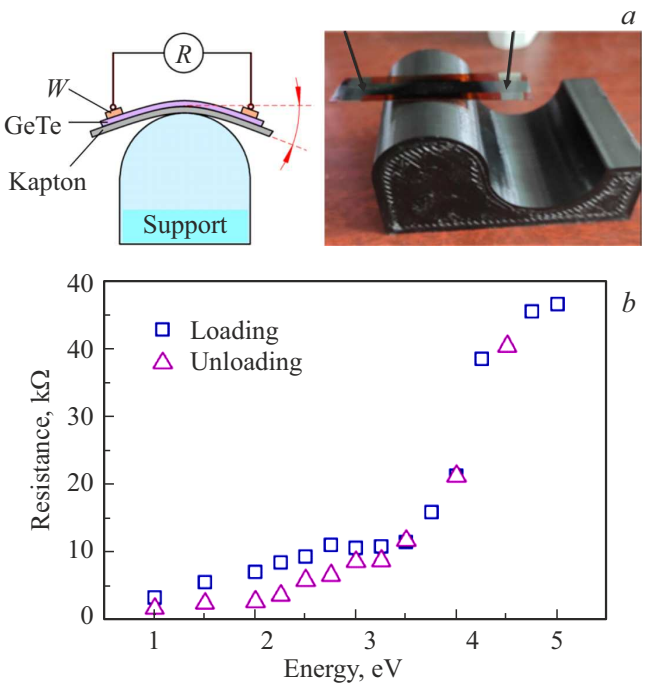

Figure 3. Scheme of experiment (a) and reversible change of conductivity when crystallized GeTe film is bent on kapton substrate (b).

causes reversible change of its electric properties. The result may be related to phenomena of „strain engineering“, when homogeneous deformations are accompanied with changes in the width of the prohibited zone and structure of the conduction band, and which, naturally, also happen and are pronounced in case of heterogeneous deformation under the flexoelectric effect, specially in narrow-gap GeTe.

The found flexoelectric effect in GeTe is especially interesting due to the presence of giant Rashba effect in GeTe [16–19]. The Rashba split value in GeTe is $k_R = 0.14\,\text{Å}^{-1}$, which is much higher than in other materials demonstrating Rashba effect. It was predicted that semiconductors with Rashba effect contain an organic link between ferroelectric polarization and chirality of spin in Rashba states, which makes it possible to control the spin transport due to manipulation of ferroelectric polarization. Conversion of spin current into charge one was demonstrated experimentally [55], besides, it was demonstrated both theoretically and experimentally how GeTe spin rotates due to change in ferroelectric polarization [56,57], which makes it possible to control the spin state by applying electrical current. The results obtained in this paper make it possible to propose a new — mechanical — method to control spin properties.

4. Conclusion

This paper, using the ab initio calculations, shows how flexoelectric polarization of order $1.0\,\mu\text{C/cm}^2$ arises in a bent thin GeTe plate, and the order of the value is comparable to the value of spontaneous polarization in rhombohedral GeTe of the same thickness. The effect seems to be especially interesting since GeTe contains giant Rashba effect, as it enables mechanical control of spin properties, which is definitely interesting for design of new spintronics devices.

The obtained ab initio estimate of the value of spontaneous polarization of volume rhombohedral GeTe phase provides value $\sim 49\,\mu\text{C/cm}^2$, which is comparable to experimental values of spontaneous polarization of model ferroelectric materials, such as $BaTiO_3$ ($26\,\mu\text{C/cm}^2$), $KNbO_3$ ($30\,\mu\text{C/cm}^2$), $LiNbO_3$ ($71\,\mu\text{C/cm}^2$), $LiTaO_3$ ($50\,\mu\text{C/cm}^2$).

It is also demonstrated that bend deformation causes substantial change in optical parameters of crystalline GeTe, which, in a combination with pronounced optical contrast of properties between crystalline and amorphous states, opens new functional opportunities of germanium telluride when developing memory cells and elements of active photonics based on phase-change materials, and also for use in flexible electronics.

The dependence of resistance on film bend related to its deformation that was observed may be caused by both homogeneous stresses arising in the film and their gradients. To separate the contribution of flexoelectric effect, additional experiments are necessary, in particular, for transition current measurements.

Funding

The paper was prepared with partial support of the Russian Research Fund (grant 22-19-00766); some calculations were made on a supercomputer of Ioffe Institute.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by M.Verenikina