Torsional Strain of TaS_3 Whiskers on the Charge-Density Wave Depinning

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We find that an electric current I exceeding the threshold value results in torsional strain of o-TaS_3 samples with one contact freely suspended. The rotation angle $\delta\phi$ of the free end achieves several degrees and exhibits hysteresis as a function of I. The sign of $\delta\phi$ depends on the I polarity; a polar axis along the conducting chains (the c axis) is pointed out. We associate the effect with surface shear of the charge-density wave (CDW) coupled to the crystal shear. The current-induced torsional strain could be treated in terms of enormous piezoelectric coefficients ($>10^{-4}$ cm/V) corresponding to shear. In essence, TaS_3 appears to be a ready torsional actuator based on the unique intrinsic property of the CDW.

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Substantial progress in understanding the properties of the charge-density wave (CDW) in quasi-one-dimensional conductors has been achieved on considering the CDW as an electronic crystal developing inside the host lattice [1]. Deformations and metastable states are intrinsic features of the CDW body [1]. One can create uniform in average (thermally-induced) or nonuniform along the sample (e.g., electric-field induced) CDW deformations. A more recent understanding is that the CDW deformation can result in a deformation of the crystal. First, the interaction was observed indirectly, as softening of the lattice—decrease of the Young modulus, Y, up to 4%, [2–7] and of the shear modulus, G, up to 30% [7–10] on the CDW depinning. According to [2], the lattice and the CDW could interact as two springs connected somehow. If so, pinned CDW contributes to the sample elastic modulus. Once depinned, the CDW rapidly relaxes, and its elastic contribution drops out [2].

Imagine another situation: the CDW is deformed by an external force. Due to the interaction of the two "springs," the crystal will change its dimensions, to enable the CDW to approach its equilibrium. This was experimentally observed as metastable length states resulting from the application of an electric field [11] or thermocycling [6]. Thus, length change on the CDW strain or compression can be directly put into correspondence with the drop of Y on CDW depinning. By analogy, what kind of effect could correspond with the G drop? The shear modulus has been studied by the method of torsional oscillations around the chain direction [8–10]. So, the first expectation is to observe torsional electric-field induced deformation. However, torsional strain corresponds with *nonuniform* shear deformation in *different* planes parallel to the chains, its value growing proportionally to the distance from the rotation axis, whereas uniform shear would correspond to a change of the interface angle (parallelogram-type distortion) in some plane parallel to the chains. Further, one should find a mechanism transforming the axial (in-chain) field or CDW deformation into rotating force and a reason for the clockwise—counter-clockwise asymmetry.

In the present Letter, we report torsional strain of needle-like TaS_3 samples developing under electric field E above the threshold for the CDW depinning, E_t, and suggest answers to the above questions. The torsional deformation appears to couple with nonuniform CDW deformation; it reveals surface pinning and development of a polar axis along the chains direction (the longer dimension of the whisker)—the c axis, likely due to a ferroelectric- or ferroelastic-type transition. Up to our knowledge, we demonstrate the first torsional actuator, in which the torque is the intrinsic property of the working element: it is not achieved by special configuration of elements ([12] and Refs. therein) or an external force ([13] and Refs. therein).

For the experiment, we selected orthorhombic TaS_3 samples from a high-quality batch—$E_t \lesssim 0.3$ V/cm. This compound showing CDW transition at $T_P = 220$ K is widely studied [1] and is known to exhibit pronounced effects of the CDW on the host lattice [6,7]. We selected samples with the cross-section areas in the range 5–300 μm^2 and prepared contacts separated by about 3 mm. The sample surfaces under both contacts were covered with gold deposited by the laser ablation technique. One of the contacts was made of indium with the usual cold-soldering technique and fixed at the substrate, so that the other end of the sample was suspended above the substrate (Fig. 1). The contact to the hanging end was provided by a long thin (typically 10×0.2 μm^2) wire soldered with a conducting epoxy. As the wires, thin whiskers of the high-T_c superconductor $Ba_2Sr_2CaCu_2O_x$ (BSCCO) or $NbSe_3$ were used.

The configuration described allows nearly free torsional strain of the samples. We studied the deformation tracing the deflection of the laser beam reflected from the sample (inset to Fig. 1). With this purpose, one or several micromirrors made, but again, from laser-cut BSCCO whiskers with golden films, were stuck to the samples. The samples were placed in an optical cryostat; heating by the laser was <1 K to minimize effect on the rotation observed. Sweeping the current through the sample, we measured its rotation angle ϕ (see [14] for the techniques details)

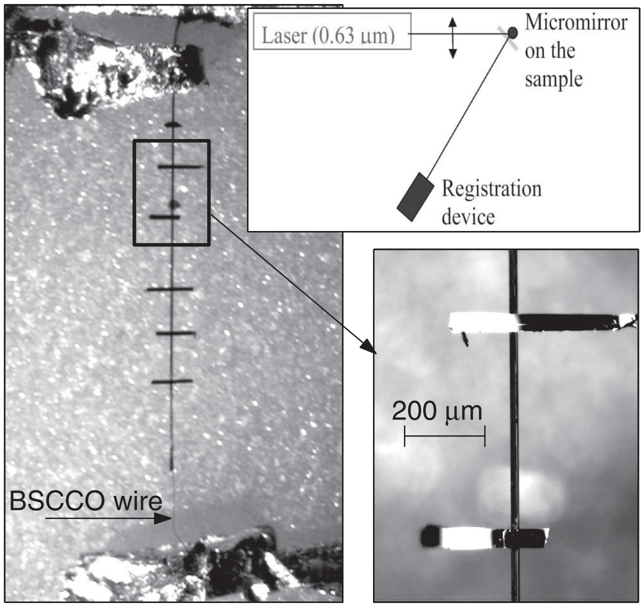

FIG. 1. Left: A microphotograph of a TaS_3 sample with a suspended contact and 6 micro-mirrors attached. The contact separation is 3.4 mm. Right: An enhanced fragment of the same sample. *Inset*: scheme of the ray path.

simultaneously with the differential resistance, R_d, measured with the conventional lock-in technique.

For all the 13 samples studied, we observed rotation of the mirrors by $\sim 1^{\circ}$ at $T = 79 \div 84$ K under application of electric field. This result indicates torsional strain of the samples. The samples rotate around the c axis, no substantial vertical shift of the reflection is seen.

Figure 2 shows typical $\delta\phi(I)$ [15] and $R_d(I)$ dependences for two TaS_3 samples about 3 mm long. In both cases, the mirror is attached near the suspended contact.

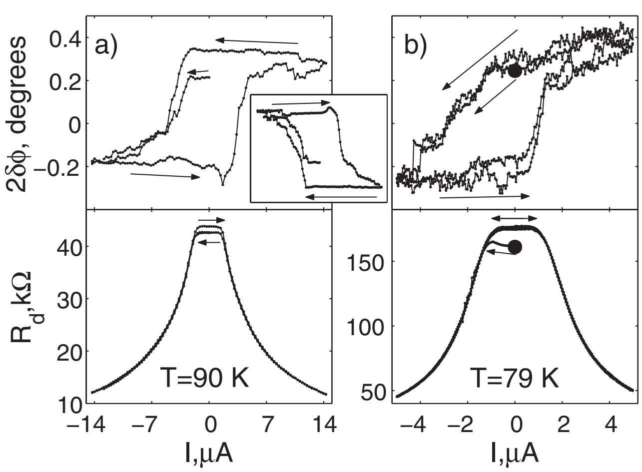

FIG. 2. $\delta\phi(I)$ and $R_d(I)$ dependences measured simultaneously. (a) and (b)—data for 2 different samples, the $\delta\phi$ scale is common. *Inset* to (a) shows the $\delta\phi(I)$ curve for the sample from the same parent crystal with the c axis turned over (arbitrary units). In (b), the initial points ($I = 0$)—the overcooled state—are marked with dark circles.

The arrows show the direction of current sweep. One can see hysteresis loops in $2\delta\phi(I)$ about 0.5° wide. The changes of ϕ begin when the voltage is approaching the threshold. The most abrupt changes of $\phi(I)$ occur at currents slightly exceeding the threshold, then $\delta\phi(I)$ saturates or depends much weaker. The metastability of the sample torsional state at zero current correlates with the torque "shape memory" of applied torsion force reported in [9] and argues that the ϕ variation, or at least the principal part of it, is coupled to the CDW deformation, rather than to its dynamics. Alternatively, the elastic hysteresis could indicate a ferroelastic-type transition [16].

Note that the sign of $\delta\phi$ depends on the current direction. Thus, the torsional deformation cannot be attributed to a stress of the sample: according to [8,9,17], G drops for both current polarities, so, one could expect the same sign of $\delta\phi$ at positive and negative currents. Similarly, Joule-heating origin of $\delta\phi$ rules out. We did not find a systematic correlation between the rotation direction and current polarity: 6 of 12 samples turned in one direction, and 6—in the opposite for the same current polarity. This could be expected: mentally turning a sample over, one shall see that the same sign of $\delta\phi$ will happen for the opposite polarity. In other words, the effect could be observed only in the case of inequivalence of the sample ends. The randomness of the rotation direction indicates that this inequivalence cannot be attributed to the difference in the contacts type.

An asymmetry of the sample ends is also revealed by the small loop on the $R_d(V)$ dependences [Fig. 2(a)] [11]. However, comparing the $\delta\phi(V)$ and $R_d(V)$ loops for different samples, we did not find a correlation between their values and signs. Most likely, the inequivalence of the two current directions revealed by the $R_d(V)$ loop does not concern the sign of $\delta\phi(V)$.

Another reason for the rotation observed could be a crystallographic asymmetry between the two directions along the c axis. Though the structure of TaS_3 has not been determined (the elementary cell comprises 24 chains), the point group is stated to be 222 [1]. In this case, one can expect shear piezoelectric deformation in the ab plane if voltage is applied along c [18]. However, the torsional strain observed is associated with the shear in the planes parallel to the c axis. So, the deformation observed *cannot* be related to the symmetry group of the sample, unless TaS_3 undergoes a ferroelectric transition.

To check the correlation of the rotation direction with the direction of the c axis, we cut a TaS_3 whisker perpendicular to the chains and turned one of the pieces by 180° so that its c axis appeared turned over. The two samples were positioned nearby on the same substrate, like the one in Fig. 1. The rotation directions appeared *different* for the same current polarity—see Fig. 2(a) and the *inset* to it as an example. This result was reproduced for 4 pairs of whiskers. If TaS_3 has a polar axis, this could be expected in the context of the c axis orientations. Moreover, the axis direction appears to be predefined in the normal state, which could be explained by a defect extended along the sample (probably, its direction is defined by the growth). Alternatively, TaS_3 could be not in the 222 point group.

We would like to emphasize that all the possible explanations having screw symmetry (a chiral axis [19], a screw dislocation [20,21]) contradict the sign change of the torsional deformation on the sample turnover.

To examine the kind of the internal force arising from the CDW deformations, it would be important to study the torsion distribution along the samples. The multimirror configuration (Fig. 1) allows us to do this. We found that all parts of the sample are turning in the same direction, the amplitude of $\delta\phi$ growing with the mirror distance, x, from the fixed probe. The dependencies of the $\delta\phi$ amplitude (i.e., the width of the $\delta\phi(I)$ loop at $I = 0$) on x shown in Fig. 3, appear roughly linear. Similarly, shifting step by step the immobile contact towards the suspended one, we found that the $\delta\phi$ amplitude falls approximately proportional to the sample length.

The dependence of $\delta\phi$ amplitude *vs.* T appears rather strong: with T decrease, it grows in average with the activation energy about 400 K—half the Peierls gap. This behavior is quite different from that of the length hysteresis loop [6], whose maximum is achieved around 100 K, and then falls gradually [22] (the measurements [22] were performed down to 35 K). The result indicates that the twisting can couple with the low-temperature anomalies [1], probably the lock-in, or the glass transition [23] (which, in turn, might be related to the commensurability [23]): note that the same activation energy, 400 K, is reported for the so-called β-process ($T < 60$ K) [23].

The $\delta\phi$ amplitude decreases with the growth of the sample width w (Fig. 4). This could be expected: at fixed torque, $\delta\phi \propto w^{-4}$ ([24], e.g.). We can consider a rotating force acting uniformly either in a layer near the surface or throughout the volume (the case of thin samples). In the first case, the torque should be proportional to w, in the 2nd—to w^2. Thus, one can expect $\delta\phi \propto w^{-3}$ or w^{-2}, which does not contradict the experiment (Fig. 4).

The frequency dependence of the $\delta\phi(f)$ amplitude needs a separate study. We noticed a slight decrease of $\delta\phi$ with growing f even for the slowest sweeps ($f \sim 10^{-3}$ Hz). However, narrow resonance peaks $\delta\phi(f)$ for f up to 10 kHz indicate a fast response of the sample.

What kind of CDW deformation gives rise to the torsional deformation? Clearly, electric field results in nonuniform CDW deformation along the sample, in contrast with roughly uniform deformation induced by thermal cycling. The latter gives a much higher variation of resistance and other sample properties, including length [6]. E.g., the value of relative length change due to the uniform CDW deformation in TaS_3 achieves $\delta L/L = 5 \times 10^{-5}$ with $\delta R/R$ exceeding 30%, while electric-field induced metastability gives $\delta L/L$ only $\sim 10^{-6}$ with several percent $\delta R/R$ [11]. In contrast, only a negligible hysteresis, within 0.1°, in $\delta\phi(T)$ was detected, while $\delta R/R$ achieved 30% against the <3% hysteresis in $\delta R/R$ *vs.* I. The same is illustrated by Fig. 2(b). At $V = 0$ (before starting the data acquisition), the current sweep was stopped, and the sample was heated by about 25 K by the laser and then cooled down. While the overcooled nature of the obtained state is obvious from the reduced value of R, no effect is seen on the $\delta\phi(I)$ dependence. Evidently, the observed torsional strain is somehow coupled to the nonuniform part of the CDW deformation. This could be the gradient of the CDW wave vector dq/dx related to the contact pinning [1]. However, as torsional strain implies high deformation of the crystal at the surface, it is more logical to relate the underlying CDW deformation to surface pinning, which can give rise to shear deformations of the CDW in the planes parallel to the c axis [25]. This assumption also agrees with the $\delta\phi$ distribution along the sample (Fig. 3). Up to our knowledge, it is the first observation of an effect of metastability related solely to nonuniform CDW deformation.

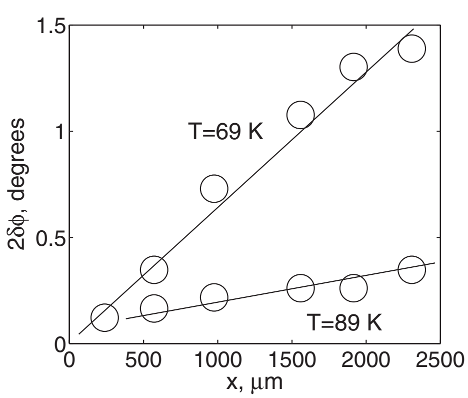

FIG. 3. Dependences of $\delta\phi(I)$ amplitude on the distance from the fixed contact for 2 temperatures indicated in the plot. A sawtooth 0.1 Hz sweep of voltage with amplitude well above the threshold current was applied.

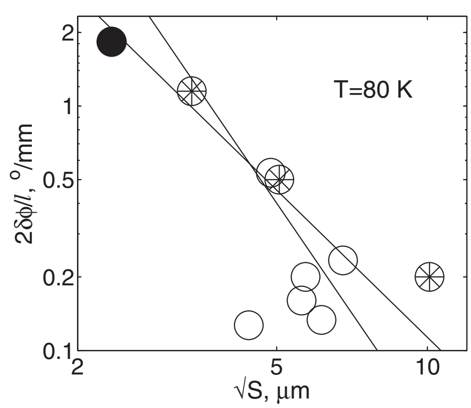

FIG. 4. $\delta\phi$ amplitude normalized by the sample length l *vs.* $w \equiv \sqrt{S} = (\rho_{300} l/R_{300})^{1/2}$, where $\rho_{300} = 3\ \Omega\ \mu$m. $l = 0.82$ mm for the thinnest sample (studied with another technique [14])—the dark circle, and $l \approx 3$ mm for the other samples. The circles marked with stars correspond to 3 different pieces of one parent sample. The solid lines show $\delta\phi \propto w^{-3}$ and $\delta\phi \propto w^{-2}$.

The estimate $\delta\phi\frac{w}{l}$ gives shear at the sample surface $\sim 10^{-4}$ and more. Dividing it by the electric field applied, we find that the deformation is equivalent to that of a piezoelectric with the piezomoduli d_{16} and d_{15} exceeding 10^{-4} cm/V (index "1" corresponding to the c axis direction).

What is the physical nature of such an enormous effect? A possible reason could be the variability of the S-S bond lengths with transferring electrons between the Ta and S atoms [26]. This feature of trichalcogenides is plausible for the explanation of coupling of the elastic properties [7] and deformations [6,11] with the longitudinal component of the q-vector. Alternatively, commensurability along the c axis would provide direct coupling of the shear deformations of the CDW and the lattice. Surface pinning naturally gives shear in the planes parallel to the c axis and perpendicular to the crystal face. If a component of shear parallel to the face appears, it would result in torsion around the c axis. This component can arise due to the symmetry loss of the TaS_3 lattice. We can assume that the low-T anomalies—a maximum of dielectric constant [23], a lock-in transition, hysteresis in elastic properties—can be the manifestations of a distributed [27] ferroelectric (ferroelastic) transition [16].

In conclusion, we have observed electric-field induced torsional strain corresponding with enormous shear in whiskers of TaS_3. The threshold and hysteretic behavior of the torsion demonstrates its coupling with the CDW deformation. The sample deformation indicates surface pinning of the CDW and is induced only by nonuniform CDW deformation. The most puzzling result is the indication of a polar axis in TaS_3. The strong $\delta\phi(T)$ dependence, different from that of $\delta L(T)$ [6,22], could indicate a relation of the torsional strain to the glass [23] or/and the lock-in [1] transitions. Detailed structural studies of TaS_3 at low temperatures could be very promising. The particular kind of CDW deformation inducing the torsion needs further clarification. The sample configuration (Fig. 1) appears to be a working torsional actuator, unique in the sense that the rotation moment arises from the intrinsic properties of the CDW.

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[1] G. Grüner, in *Density Waves in Solids* (Addison-Wesley, Reading, MA, 1994); P. Monceau, in *Electronic Properties of Inorganic Quasi-One-Dimensional Conductors*, edited by P. Monceau (Reidel, Dortrecht, 1985), p. 139, Part 2; *International Conference on Electronic Crystals* [J. Phys. IV (France) 131 (2005)].
[2] G. Mozurkewich, Phys. Rev. B **42**, 11 183 (1990); L. C. Bourne and A. Zettl, Phys. Rev. B **36**, 2626 (1987).
[3] J. W. Brill and W. Roark, Phys. Rev. Lett. **53**, 846 (1984); X.-D. Xiang and J. W. Brill, Phys. Rev. B **36**, 2969 (1987).
[4] R. L. Jacobsen and G. Mozurkewich, Phys. Rev. B **42**, 2778 (1990).
[5] Z. G. Xu and J. W. Brill, Phys. Rev. B **45**, 3953 (1992).
[6] A. V. Golovnya, V. Ya. Pokrovskii, and P. M. Shadrin, Phys. Rev. Lett. **88**, 246401 (2002).
[7] J. W. Brill, in *Handbook of Elastic Properties of Solids, Liquids, and Gases*, edited by M. Levy, H. E. Bass, and R. R. Stern (Academic, New York, 2001), Vol. II, pp. 143–162.
[8] X.-D. Xiang and J. W. Brill, Phys. Rev. B **36**, 2969 (1987).
[9] X. Zhan and J. W. Brill, Phys. Rev. B **52**, R8601 (1995).
[10] A. J. Rivero, H. R. Salva, A. A. Ghilarducci, P. Monceau, and F. Levy, Solid State Commun. **106**, 13 (1998).
[11] S. Hoen, B. Burk, A. Zettl, and M. Inui, Phys. Rev. B **46**, 1874 (1992).
[12] Jaehwan Kim and Byungwoo Kang, Smart Materials and Structures **10**, 750 (2001).
[13] T. D. Yuzvinsky, A. M. Fennimore, A. Kis, and A. Zettl, Nanotechnology **17**, 434 (2006).
[14] S. G. Zybtsev, V. Ya. Pokrovskii, and A. P. Kuznetsov, *Scientific Seccion of MEPI* (MEPI, Moscow, 2007), Vol. 4, p. 37.
[15] Actually, $2\delta\phi$ is plotted—the angle of the beam deflection, twice the sample turning.
[16] See T. M. Tritt, M. Marone, A. C. Ehrich, and M. J. Skove *et al.*, Phys. Rev. Lett. **68**, 2531 (1992) and references therein.
[17] J. W. Brill (private communication).
[18] J. F. Nye, *Physical Properties of Crystals. Their Representation by Tensors and Matrices* (Oxford at the Clarendon Press, Oxford, 1964).
[19] Haiyi Liang and Moneesh Upmanyu, Phys. Rev. Lett. **96**, 165501 (2006).
[20] D. Le. Bolloc'h *et al.*, Phys. Rev. Lett. **95**, 116401 (2005).
[21] J. C. Gill, Synth. Met. **43**, 3917 (1991).
[22] A. V. Golovnya and V. Ya. Pokrovskii (unpublished).
[23] D. Staresinic, K. Biljakovic, W. Brutting, K. Hosseini, P. Monceau, H. Berger, and F. Levy, Phys. Rev. B **65**, 165109 (2002).
[24] J. M. Gere and S. P. Timoshenko, *Mechanics of Materials* (Chapman & Hall, London, 2000), p. 808.
[25] T. Tamagai *et al.*, Solid State Commun. **51**, 585 (1984); R. M. Fleming *et al.*, Phys. Rev. B **31**, 4099 (1985).
[26] A. Meerschaut, J. Phys. (France) **44**, C3-1615 (1983).
[27] In the case of the exponential approach of the q-vector to $c^*/4$ [S. N. Artemenko, V. Ya. Pokrovskii, and S. V. Zaitsev-Zotov, Zh. Eksp. Teor. Fiz. **110**, 1069 (1996) [JETP **83**, 590 (1996)] one can expect a distributed lock-in transition.