Coupling of the Lattice and Superlattice Deformations and Hysteresis in Thermal Expansion for the Quasi-One-Dimensional Conductor TaS_3

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An original interferometer-based setup for measurements of length of needlelike samples is developed, and thermal expansion of o-TaS_3 crystals is studied. Below the Peierls transition the temperature hysteresis of length L is observed, the width of the hysteresis loop $\delta L/L$ being up to 5×10^{-5}. The behavior of the loop is anomalous: the length changes so that it is in front of its equilibrium value. The hysteresis loop couples with that of conductivity. With lowering the temperature down to 100 K the charge-density waves' elastic modulus grows achieving a value comparable with the lattice Young modulus. Our results could be helpful in consideration of different systems with intrinsic superstructures.

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Internal degrees of freedom is a feature of a random system; in principle, they can give rise to metastable size states resulting, say, in hysteresis in thermal expansion [1]. A special class is formed by the compounds with intrinsic superstructures. Comprising two periodicities, generally incommensurate, the compounds occupy an intermediate place between genuine aperiodic and truly periodic systems [2]. In these systems, such as charge- and spin-density waves (CDW and SDW) [3], Wigner crystals, superconductors in magnetic fields [4], and structurally incommensurate crystal phases [5], the superstructure periodicities could be varied by external fields or temperature changes. The resulting metastable configurations can be reflected back onto the elastic properties and size of the underlying lattice [3–5], though this question is still poorly understood.

Quasi-one-dimensional conductors with CDW belong to a widely studied class of materials, in which intrinsic superstructure develops through the Peierls transition [6]. When electrons condense into CDW they form a deformable medium—an electronic crystal. Deformation of the CDW affects their main static and dynamic properties and gives rise to metastability and hysteresis.

The straightforward treatment of the CDW as a spring, whose strain is just applied to the crystal at the ends or via the impurities is not valid. Moreover, in the simple one-dimensional model the strains of the CDW and the crystal do not couple at all: if initially the CDW are relaxed, any change of the crystal length would not draw the CDW away from the equilibrium, i.e., give rise to a CDW deformation [7], as was noticed in Refs. [8–11]. Similarly, once the CDW is deformed, any change of the lattice constant, c, would neither decrease nor increase the deviation of the CDW wavelength λ from the equilibrium value, λ_{eq}. So, within this model a CDW deformation would not give rise to a length change.

At the same time, the interaction of the CDW and the lattice is clearly seen from the elastic anomalies, including a drop of the Young modulus of the lattice [8–11], Y_l, up to 4% [10], when the CDW become depinned. Mozurkewich [8] has concluded that the lattice deformation *does* give rise to a deformation of the CDW: when the CDW are at rest, they cannot relax, and so they contribute to the total elastic energy; the sliding CDW relax rapidly and their contribution drops out [8]. For his model Mozurkewich [8] introduced an empirical parameter g reflecting the deviation of λ_{eq} from the simple one-dimensional model:

$$\delta\lambda_{eq}(c)/\lambda_{eq}(c_{eq}) = (g + 1)\delta c/c_{eq}, \qquad (1)$$

$g \neq 0$. However, no way was proposed to estimate g.

Another remarkable observation was reported in Ref. [12]: the length L of TaS_3 samples as a function of electric field demonstrated hysteresis partly scaling with that of resistance. The values of L obtained at different directions of the voltage sweep differed by $\sim 10^{-6}$. This result was also treated in terms of coupling of the CDW strains with the deformation of the pristine lattice. Note that the field-induced length change (as well as the change of resistance) results only from an inhomogeneity of the sample properties: obviously, the length could depend on the voltage polarity only if the inversion symmetry of the sample is broken [12]. Thus, study of the *electric-field* induced hysteresis of length cannot provide complete understanding of the CDW-lattice coupling.

To study the effect of the CDW deformation on the crystal length it could be more fruitful to observe *thermal* hysteresis of L. With changing temperature the q vector ($q \equiv 2\pi/\lambda$) falls *behind* its equilibrium value, which is temperature dependent [13]; the deviation of q from the equilibrium is limited by the critical deformation at which the phase slippage (PS) begins [14]. So, thermal cycling creates a CDW deformation, which is relatively uniform along the sample and is of the maximum possible value.

For our study we chose o-TaS_3 as a representative CDW conductor. Among the quasi-one-dimensional conductors TaS_3 is one of the most widely studied, including the elastic properties. TaS_3 demonstrates the Peierls transition at $T_P = 220$ K, below which the resistance follows an activation law revealing the half-gap $\Delta = 700$ K. The

dependence $R(T)$ demonstrates a pronounced hysteresis, the width of the loop $\delta R/R$ being up to 50% at T around 100 K.

In the present Letter we report temperature hysteresis of length for o-TaS_3; the hysteresis couples with that of resistance having an anomalous sign. A quantitative treatment of the effect is proposed.

We studied samples of TaS_3 with typical length 1 mm, width 15–35 μm, and thickness 5–10 times less. The samples were arranged on a transparent glass substrate (Fig. 1a). The contacts were fixed on the substrate with indium, while the central part of the sample formed an arc. The inner surface of the substrate played the role of a semitransparent mirror. The laser beam with wavelength $\lambda_l = 635$ nm fell down through the substrate and partially reflected from the inner surface of the substrate and from the sample surface forming an interference pattern (similar with the wedge interference). The pattern was fixed with a video camera combined with a microscope. An example of such a pattern is shown in Fig. 1b. The neighboring dark or bright fringes correspond with change of the sample distance y from the substrate surface by $\pm\lambda_l/2$. Making sections of such images (an example is shown in Fig. 1c) we obtained the profiles $y(x)$ of the samples, such as the curve presented in Fig. 1d. Finally, the length of such curves was calculated. We detect a length change about 5 Å which corresponds to the relative length change $\delta L/L = 5 \times 10^{-7}$, though in principle the sensitivity could be improved [15]. Our estimates have shown that the contributions to δL due to the changes of stress and Y_l are negligible [16]. Thus, the observed changes of L with temperature were associated with the change of the equilibrium sample length with respect to the substrate. To have absolute results we have measured the thermal expansion of the glass substrate in addition.

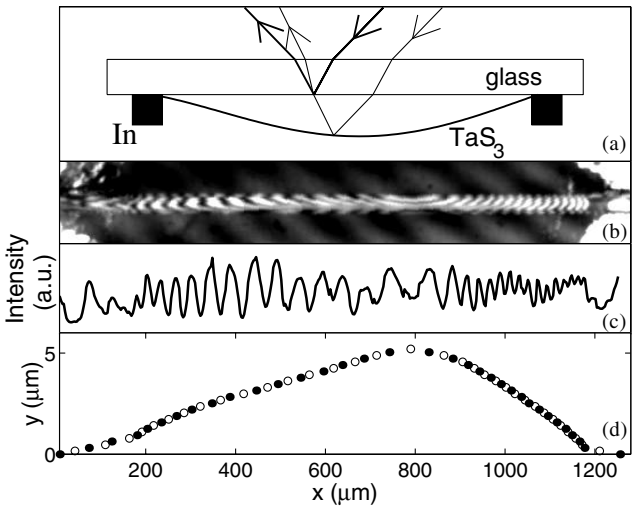

FIG. 1. (a) Arrangement of a TaS_3 sample on the substrate and the scheme of the reflections and interference of the laser beams (the incidence is close to normal). (b) An example of an image obtained. (c) The section of the image. (d) The resulting profile of the sample. The open circles correspond to the minima in the section (c) and the closed circles to the maxima.

Figures 2a and 2b show the temperature dependences of length (with respect to glass) and of the resistance for the representative sample of TaS_3. In the inset of Fig. 2a the absolute dependence of length is shown [18]. The dependences of length and resistance both clearly show hysteresis below the Peierls transition temperature $T_P = 214$ K. The length hysteresis loop opens immediately below T_P. The development of hysteresis is the dominating effect near T_P, on whose background it is difficult to distinguish a feature coupled to the transition in itself [19]. The length hysteresis grows below T_P achieving $\delta L/L = 5 \times 10^{-5}$ (Fig. 2a), which by 1.5 orders of magnitude exceeds the maximum value reported in Ref. [12]. At the same temperature the states approached from lower temperature have higher length than those approached from above. Correspondingly, application of the electric field exceeding the threshold reduces the length after heating the sample and increases after cooling. Thus, the main effect of the electric field is the relaxation of the thermally induced

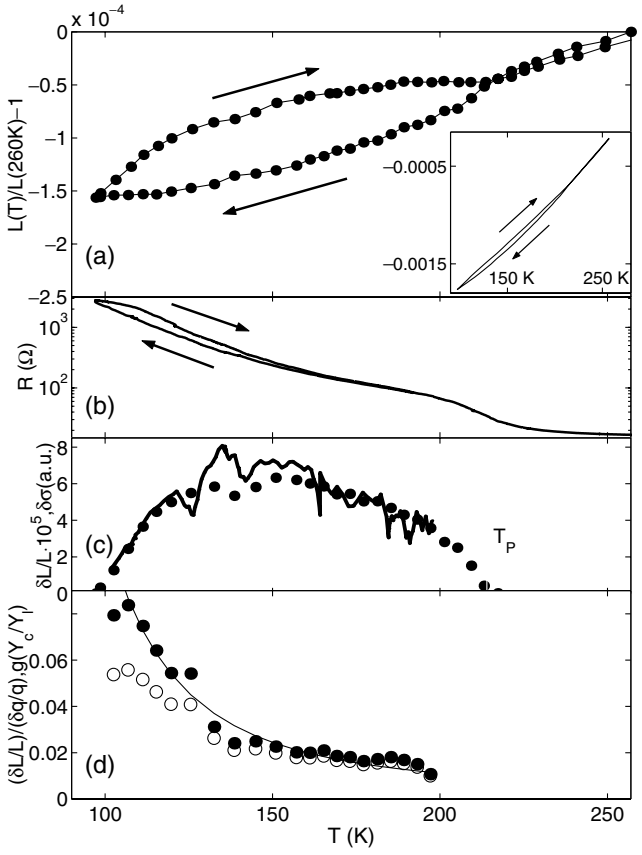

FIG. 2. (a) Temperature dependence of $\delta L/L$ with respect to glass. The absolute thermal expansion is shown in the inset. (b) $R(T)$ measured simultaneously. (c) The width of the length (the circles) and conductivity (the solid line) hysteresis loops as a function of T. (d) The ratio $(\delta L/L)/(\delta\lambda/\lambda)$ (open circles) and gY_c/Y_l (black circles) resulting from (c). We use Eq. (3) and the $\mu(T)$ dependence [17]. The solid line indicates $Y_c \propto \exp(470/T)$.

states. The length change induced by the field in itself was $\sim 10^{-6}$, as in Ref. [12]. Note that the sign of the hysteresis is nontypical: the length is *in front* of its equilibrium value (inset to Fig. 2a), but not behind.

The length hysteresis apparently couples with the resistance hysteresis, the higher length corresponding to a higher resistance at a given temperature [20]. The coupling between R and L is well seen from Fig. 2c, where the temperature dependence of $\delta L/L$ is presented together with the loop of conductivity, $\delta\sigma \equiv 1/R_{\rm cool} - 1/R_{\rm heat}$. Note that in the unipolar approximation $\delta\sigma \approx \sigma_{300}(\delta\lambda/\lambda)(\mu/\mu_{300})$ [21], where the index "300" marks the room-temperature values. So, the σ hysteresis reflects that of the CDW wavelength to the accuracy of the temperature dependence of the mobility μ, which in turn can be found from Ref. [17]. Figure 2d shows the ratio $(\delta L/L)/(\delta\lambda/\lambda)$ vs T. At the low temperatures $\delta L/L$ is $\sim$6% of the CDW deformation.

As we have noticed in the beginning, the interactions of the CDW and the sample cannot be presented as that of two springs connected in parallel (the lower inset in Fig. 3). Though we do not see a way to obtain quantitatively the strain dependence of the q vector for TaS_3, one can recall experimental results, from which it is possible to estimate the value of g [Eq. (1)]. It has been found [22] that at a certain value of uniaxial strain S^* the properties of the CDW change abruptly: e.g., the nonlinear conduction nearly disappears. This has been attributed to the transition of the CDW to the fourfold commensurability. Comparing the normalized dependences of the q vector [13] and of the strain S^* [22] on temperature (Fig. 3) one can see that they become similar [22] if one multiplies the value of S^* by 6. Thus, one can assume that a deformation of the lattice induces the change of the equilibrium CDW wavelength $\lambda_{\rm eq}(c)$ in accordance with Eq. (1) with $g \approx 6$. Such a large value of g indicates that the simple one-dimensional model [7] cannot even roughly describe the strain-induced change of $\lambda_{\rm eq}$. Evidently, the change of $\lambda_{\rm eq}$ is dominated by transverse effects: the longitudinal strain decreases the thickness of the sample resulting in an increase of the intrachain coupling. This modifies the form of the Fermi surfaces and, consequently, the q vector [22]. To comprehend the sign and the value of the q change one should study the evolution of the Fermi surface in detail. In principle, we cannot exclude that g is temperature dependent. However, as we see below, the assumption that $g = \text{const}$, namely, $g \approx 6$, is consistent with our experiment.

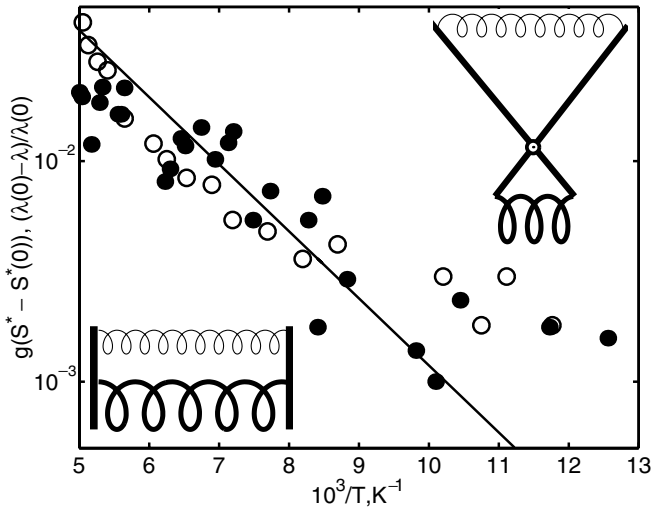

FIG. 3. The temperature dependences of $S^* - S(0)$ (open circles) [22] and of the wave vector [13] $[q - q(0)]/q(0)$ (closed circles) [23]. S^* is multiplied by $g = 6$. Insets: the equivalent schemes illustrating the interaction of the CDW (the thin-line spring) and the pristine lattice (the thick-line spring). The lower-left sketch is the naive scheme, which is invalid. The upper-right sketch illustrates Eq. (3) ($g > 1$).

For the next step, we present the elastic energy density W as a sum of the lattice and the CDW energies:

$$W = \frac{1}{2}\left[Y_l\left(\frac{c - c_{\rm eq}}{c_{\rm eq}}\right)^2 + Y_c\left(\frac{\lambda - \lambda_{\rm eq}(c)}{\lambda_{\rm eq}}\right)^2\right], \quad (2)$$

where Y_l and Y_c are the elastic moduli of the lattice and the CDW, respectively. Taking into account the condition (1) [24] and assuming that no PS occurs ($\lambda/c = \text{const}$), we can minimize W and obtain the resulting length change:

$$\frac{\delta L}{L} = \frac{\delta c}{c_{\rm eq}} = g\,\frac{Y_c}{Y_l + g^2 Y_c}\,\frac{\delta\lambda}{\lambda} \approx g\,\frac{Y_c}{Y_l}\,\frac{\delta\lambda}{\lambda}, \quad (3)$$

where $\delta\lambda$ is the initial CDW deformation (at fixed c). The approximation implies that $g^2 Y_c \ll Y_l$. Equation (3) is quite transparent: the crystal deforms as a spring connected in parallel to the CDW, but with a factor $-g$. $g > 0$ means that, say, compressed CDW ($\lambda < \lambda_{\rm eq}$) would result in a decrease of the sample length, which agrees with our observation. E.g., cooling corresponds to the growth of $\lambda_{\rm eq}$ [13], so the CDW is in a compressed state ($\lambda - \lambda_{\rm eq} < 0$), which results in decreased L (Fig. 2a). The CDW-crystal interaction could be illustrated with a scheme consisting of two springs connected via a lever (Fig. 3, upper inset).

From Eq. (3) it follows that the ratio $(\delta L/L)/(\delta\lambda/\lambda)$ (Fig. 2d) equals gY_c/Y_l. Note, however, that with $g = 6$, $g^2 Y_c$ at low temperatures is comparable with Y_l, and one should use the exact version of Eq. (3). The resulting value of gY_c/Y_l is also shown in Fig. 2d. One can see the growth of the CDW elastic modulus with lowering temperature, though slower than $Y_c \propto \exp(\Delta/T)$ [14,25] (see the solid line in Fig. 2d) [26]. Note that the curve $(\delta L/L)/(\delta\lambda/\lambda)$ vs T resembles the temperature dependences of the lattice softening in the electric field [10]. This could be expected, since from Eqs. (1) and (2) it follows that the value $g^2 Y_c$ is added to Y_l when the CDW are at rest, while in the sliding state the CDW contribution drops out [8].

From the condition of neutrality [25] accompanying the CDW deformation we can obtain for the CDW Young modulus: $Y_c = \frac{d\zeta}{dq}\frac{q^2}{\pi s}$ [14], where $\frac{d\zeta}{dq}$ is the derivative of

the chemical potential level by the CDW q vector, and s is the area per chain. Substituting this in Eq. (3), we obtain

$$\frac{\delta L}{L} \approx g \frac{2\delta\zeta}{\lambda s Y_l}. \quad (4)$$

For the unipolar (p-type for TaS_3) conduction [14,17] $\delta\zeta = T \ln(R_{\text{heat}}/R_{\text{cool}})$. Substituting into Eq. (4) $g = 6$, $\delta\zeta = 50$ K (for $T = 120$ K, Fig. 2b), $\lambda = 10$ Å, $s = 80$ Å^2 (Ref. [27]), $Y_l = 380$ GPa [28], we obtain $\delta L/L = 3 \times 10^{-5}$, in agreement with the experiment (Fig. 2b). This agreement supports the approach we used to estimate g and proves that under a certain uniaxial strain (S^*) the CDW in fact transit to the fourfold commensurability [22].

In conclusion, we have observed thermal hysteresis of length for the quasi-one-dimensional conductor TaS_3. In the framework of the model proposed the observed anomalous sign and value of the hysteresis loop are consistent with the dependence of the q vector on the lattice strain. The results could be helpful in understanding the behavior of other systems with intrinsic superstructures, whose parameters could be rearranged due to the temperature effects or external fields.

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[1] For a recent example, see P. Nagel, V. Plaster, C. Meingast, A. Rykov, and S. Tajima, Phys. Rev. Lett. **85**, 2376 (2000).
[2] J. Voit, L. Perfetti, F. Zwick, H. Berger, G. Margaritondo, G. Grüner, H. Höchst, and M. Grioni, Science **290**, 501 (2000).
[3] 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 Press, New York, 2001), Vol. II, pp. 143–162.
[4] V. V. Eremenko, V. A. Sirenko, H. Szymczak, and A. Nabialek, J. Low Temp. Phys. **25**, 225 (1999).
[5] H. Z. Cummins, Phys. Rep. **185**, 211 (1990).
[6] *Charge Density Waves in Solids,* edited by L. Gor'kov and G. Grüner (Elsevier Science, Amsterdam, 1989); G. Grüner, in *Density Waves in Solids* (Addison-Wesley, Reading, MA, 1994).
[7] This follows from the fact that on longitudinal deformation of a sample the number of electrons per the lattice period does not change, and $\lambda_{\text{eq}}(c)$ changes proportionally to c, i.e., $\delta\lambda_{\text{eq}}(c)/\lambda_{\text{eq}}(c_{\text{eq}}) = \delta c/c_{\text{eq}}$.
[8] G. Mozurkewich, Phys. Rev. B **42**, 11 183 (1990).
[9] J. W. Brill and W. Roark, Phys. Rev. Lett. **53**, 846 (1984); Phys. Rev. B **36**, 2969 (1987).
[10] R. L. Jacobsen and G. Mozurkewich, Phys. Rev. B **42**, 2778 (1990).
[11] Z. G. Xu and J. W. Brill, Phys. Rev. B **45**, 3953 (1992).
[12] S. Hoen, B. Burk, A. Zettl, and M. Inui, Phys. Rev. B **46**, 1874 (1992).
[13] Z. Z. Wang, H. Salva, P. Monceau, M. Renard, C. Roucau, R. Ayroles, F. Levy, L. Guemas, and A. Meerschaut, J. Phys. (Paris), Lett. **44**, L315 (1983).
[14] V. Ya. Pokrovskii and S. V. Zaitsev-Zotov, Synth. Met. **32**, 321 (1989).
[15] The interferometric methods for thermal expansion resolve 10^{-2}–5×10^{-4} of a fringe [T. H. K. Barron, J. G. Collins, and G. K. White, Adv. Phys. **29**, 609 (1980)]; in our configuration this corresponds to $\delta L/L \sim 10^{-8}$–10^{-10}.
[16] A. V. Golovnya and V. Ya. Pokrovskii (to be published).
[17] Yu. I. Latyshev, Ya. S. Savitskaya, and V. V. Frolov, JETP Lett. **38**, 541 (1983).
[18] D. Maclean and M. H. Jericho, Phys. Rev. B **47**, 16 169 (1993): the presented thermal expansion (at considerable sample strain and at high electric fields) is in rough agreement with our data.
[19] If one takes $L(T) \equiv [L_{\text{cool}}(T) + L_{\text{heat}}(T)]/2$, he will obtain a decrease of length $\sim 10^{-5}$ associated with the Peierls transition, in qualitative agreement with Ref. [18].
[20] In Ref. [12] the state with smaller L corresponded to higher R. Evidently, both the R and L changes reported [12] result from noncomplete compensation of the contact CDW deformations of opposite signs. In this case one can obtain an arbitrary relation between the R and L hysteresis dominated by the nonlinear effects. Concerning our experiment, the small difference in the forms of the loops of L and R (Fig. 2c), as well as the small loop of L above T_P (Fig. 2a), is evidently within our experimental error.
[21] D. V. Borodin, S. V. Zaitsev-Zotov, and F. Ya. Nad', Zh. Eksp. Teor. Fiz. **93**, 1394 (1987) [Sov. Phys. JETP **66**, 793 (1987)]; this relation could be easily obtained from the neutrality condition if one notes that a variation of the q vector changes the number of the states under the Peierls gap, and, thus, the number of quasiparticles.
[22] V. B. Preobrazhensky, A. N. Taldenkov, and I. Yu. Kalnova, Pis'ma Zh. Eksp. Teor. Fiz. **40**, 182 (1984) [JETP Lett. **40**, 944 (1984)]; V. B. Preobrazhensky, A. N. Taldenkov, and S. Yu. Shabanov, Solid State Commun. **54**, 1399 (1985).
[23] We took $S(0) = 3.9 \times 10^{-3}$, and $q(0) = 0.2503c^*$ suggesting that both dependences follow the Arrhenius law (the slope of the line corresponds to 700 K, which is close to Δ).
[24] Equation (2) implies that the principal part of the CDW elastic energy is associated with their longitudinal deformations, while Eq. (1) takes into account the dependence of λ_{eq} on all components of the crystal deformation.
[25] S. N. Artemenko and A. F. Volkov, Zh. Eksp. Teor. Fiz. **81**, 1872 (1981) [Sov. Phys. JETP **54**, 992 (1981)].
[26] Actually the CDW deformation is spatially nonuniform, so one can expect nonlinear effects, e.g., the reduction of Y_c at low T.
[27] P. Monceau, in *Electronic Properties of Inorganic Quasi-One-Dimensional Conductors,* edited by P. Monceau (D. Reidel Publishing Company, Dordrecht, 1985), Pt. 2.
[28] J. W. Brill, Solid State Commun. **41**, 925 (1982).