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 needle-like 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 $5 \cdot 10^{-5}$. 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. The sign and the value of the length hysteresis are consistent with the strain dependence of the charge-density waves (CDW) wave vector. With lowering temperature down to 100 K the CDW 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, to hysteresis in thermal expansion. A special class form the compounds with intrinsic superstructures. Comprising two periodicities, generally incommensurate, the compounds occupy intermediate place between genuine aperiodic and truly periodic systems. In these systems, such as charge- and spin-density waves (CDW and SDW), Wigner cristals, superconductors in magnetic fields, structurally incommensurrate crystal phases, 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, though this question is still poorly understood.

Quasi 1-dimensional conductors with CDW belong to a widely studied class of materials, in which intrinsic superstructure develops through the Peierls transition. 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, as it was noticed in Ref. The 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

Mozurkewich 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. For his model Mozurkewich introduced an empirical parameter $g$ reflecting the deviation of $\lambda_{eq}$ from the simple one-dimensional model:

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

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

Another remarkable observation was reported in Ref. 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. Thus, study of the electric-field induced hysteresis of length can not 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. The deviation of $q$ from the equilibrium is limited by the critical deformation at which the phase slippage (PS) begins. 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.

### FIG. 1

![Diagram](image.png)

**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 (Fig.1c), and the closed circles — to the maxima.

We studied samples of TaS$_3$ with typical length 1 mm, width 15–35 $\mu$m, 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 semi-transparent 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, like 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 $\Delta L/L = 5 \cdot 10^{-7}$, though in principle the sensitivity could be improved. Our estimates have shown that the contributions to $\delta L$ due to the changes of stress and $Y_l$ are negligible. 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 thermal expansion of the glass substrate in addition.

### FIG. 2

![Graph](image.png)

**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 Fig. 2c. We use Eq. 3 and the $\mu(T)$ dependence. The solid line indicates $Y_c \propto \exp(470/T)$.

Figs. 2a) and b) show the temperature dependences of length (with respect to glass) and of the resistance for the representative sample of TaS$_3$. In the inset to Fig. 2a) the absolute dependence of length is shown. 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. The length hysteresis grows below $T_P$ achieving
The length hysteresis apparently couples with the resistance hysteresis, higher length corresponding to higher resistance at a given temperature. 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, \( \delta \sigma = 1/R_{\text{cool}} - 1/R_{\text{heat}} \). Note that in the unipolar approximation \( \delta \sigma \approx \sigma_{300}(\delta \lambda/\lambda)(\mu/\mu_{300}) \) where the index “300” marks the room–temperature values. So, the \( \sigma \) hysteresis reflects that of the CDW wavelength to the accuracy of the temperature dependence of the mobility \( \mu \), which in turn can be found from Ref. 22. Fig. 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 to 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\(^2\) that at a certain value of uniaxial strain \( S^* \) the properties of the CDW change abruptly: e.g., the non-linear conduction nearly disappears. This has been attributed to the transition of the CDW to the 4-fold commensurability. Comparing the normalized dependences of the \( q \)-vector\(^2\) and of the strain \( S^* \)\(^2\) on temperature (Fig. 3) one can see that they become similar\(^2\) 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 \( \lambda_{\text{eq}}(c) \) in accordance with Eq. 3 with \( g \approx 6 \). Such a large value of \( g \) indicates that the simple 1-dimensional model\(^2\) cannot even roughly describe the strain-induced change of \( \lambda_{\text{eq}} \). Evidently, the change of \( \lambda_{\text{eq}} \) 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.\(^2\) 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 shall see below, the assumption that \( g = \text{const} \), namely \( g \approx 6 \), is consistent with our experiment.

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

\[
W = \frac{1}{2}(Y_1(\frac{c}{c_{eq}})g)^2 + Y_\varepsilon(\frac{\lambda - \lambda_{eq}(c)}{\lambda_{eq}})^2, \tag{2}
\]

where \( Y_1 \) and \( Y_\varepsilon \) are the elastic moduli of the lattice and the CDW respectively. Taking into account the condition Eqs. 1 and 2 follows that the value \( \delta \lambda/\lambda \) resembles the temperature dependences of the lattice stiffness\(^2\).

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

\[
\lambda < \lambda_{eq} < 0.
\]

The approximation implies that \( \lambda \sim 6 \). Such a large value of \( g \) means that \( \lambda_{\text{eq}} \) is comparable with \( \lambda \). Thus, one can assume that a deformation of the lattice induces the change of the equilibrium CDW wavelength \( \lambda_{\text{eq}}(c) \) in accordance with Eq. 3 with \( g \approx 6 \). Such a large value of \( g \) indicates that the simple 1-dimensional model\(^2\) cannot even roughly describe the strain-induced change of \( \lambda_{\text{eq}} \). Evidently, the change of \( \lambda_{\text{eq}} \) 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.\(^2\) 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 shall see below, the assumption that \( g = \text{const} \), namely \( g \approx 6 \), is consistent with our experiment.

For the next step, we present the elastic energy density \( W \) as a sum of the lattice and the CDW energies:
From the condition of neutrality accompanying the CDW deformation we can obtain for the CDW Young modulus: \( Y_c = \frac{\partial c}{\partial q} \frac{q^2}{\pi s} \), where \( \frac{\partial c}{\partial q} \) 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:

\[
\frac{\delta L}{L} \approx \frac{2 \delta \zeta}{\lambda s Y_c}.
\]

For the unipolar (p-type for TaS\(_3\)) conduction, \( \delta \zeta = T \ln(R_{\text{heat}}/R_{\text{cool}}) \). Substituting into Eq. 1 \( g = 6 \), \( \delta \zeta = 50 \text{ K (for } T = 120 \text{ K, Fig. 2b)} \), \( \lambda = 10 \text{ Å, } s = 80 \text{ Å}^2 \) (Ref. 27), \( Y_c = 380 \text{ GPa} \), we obtain \( \delta L/L = 3 \cdot 10^{-5} \), 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 4-fold commensurability.

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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