Peierls transition as spatially inhomogeneous gap suppression

V. Ya. Pokrovskii,* A. V. Golovnya, and S. V. Zaitsev-Zotov
Institute of Radioengineering and Electronics, Russian Academy of Sciences, 101999 Moscow, Russia
(Received 23 April 2004; published 27 September 2004)

We propose a model of the Peierls transition (PT) taking into account amplitude fluctuations of the charge-density waves and spontaneous thermally activated suppression of the Peierls gap, akin to the phase slip process. The activation results in the exponential growth of the normal phase with increasing temperature. The model fairly describes the behavior of resistance, thermal expansion, Young modulus, and specific heat both below and above the PT temperature T_P. The PT appears to have a unique nature: it does not comprise T_P as a parameter, and at the same time it has features of the first-order transition. The possible basis for the model is activation of noninteracting amplitude solitons perturbing large volumes around them.

DOI: 10.1103/PhysRevB.70.113106 PACS number(s): 71.45.Lr, 68.35.Rh, 71.30.+h

Description of the Peierls transition (PT) in quasi-one-dimensional (quasi-1D) conductors still remains a controversial problem. The widely used mean-field (MF) approach works poorly primarily because of strong 1D fluctuations. For example, it predicts the PT temperature T_P much above the observed value. Say, for the typical compound TaS_3, the energy gap 2Δ is 1600 K, and the MF value of T_P should be $2\Delta/3.5=460$ K, while the experimental value is 220 K. The large fluctuations reveal themselves well above T_P: the value of the pseudogap is close to the low-temperature value,[1,2] the threshold nonlinear conduction[3] indicates the charge-density wave (CDW) state within the fluctuating volumes. At present only qualitative attempts to explain these experimental facts are undertaken. Though certain success is achieved in fitting the behavior of different values near T_P,[4–6] the relations involved are semiempirical, and their physical sense is not quite clear. Another treatment of the PT is given by the generalized Ehrenfest relation[7] between the specific heat, expansivity, Young modulus anomalies, and stress-induced shift of the transition temperature. This relation works nicely for some materials, e.g., for $K_{0.3}MoO_3$ (the blue bronze),[4] but fails for others, such as for TaS_3.[8]

The general approach to the CDW's is to consider them as a spatially homogeneous state up to T_P. However, a recent theoretical study has demonstrated that thermal fluctuations of the CDW stress may be very large at $T \approx T_P$, so that the rms shift of the chemical potential level from the middle-gap position appears comparable with Δ,[9] and one can expect temporal local suppression of the gap. So, it is more reasonable to consider the CDW in the vicinity of T_P as a mixture of the Peierls phase (the CDW) and the state with temporary suppressed gap. Studies of noise have revealed spontaneous phase-slippage (PS) process[10,11] in the vicinity of T_P, which also implies local temporal suppression of the Peierls gap. The PS is fairly described as a thermally activated process,[12–14] so it would be intriguing to extend the approach for the description of the PT.

In the present paper we propose a model in which the fluctuations of Δ are phenomenologically introduced as thermally activated local gap suppression (LGS). With increasing T this process gives rise to the activation growth of concentration of normal phase as $\exp(-W/T)$, $W \gg \Delta$. The approach can be extrapolated above the transition temperature. PT appears to be smeared out, but at the same time has features of the first-order transition. The model appears to describe fairly the behavior of various parameters near T_P. The plausible basics for the model are the excitation of amplitude solitons perturbing considerable volumes around them.

To introduce the fluctuations, we shall use the following relation giving the frequency of the LGS acts per unit volume (see also Ref. 14):

$$f = f_a \exp(-W/T), \tag{1}$$

where f_a is an attempt frequency. Here the essential point is that each LGS act results in a temporal nucleation of the normal-state volume v_0 having certain lifetime τ. Then the fraction of the normal-state volume due to the spontaneous LGS process is

$$v = v_0 \tau f. \tag{2}$$

This fraction grows exponentially with increasing T. At high enough temperature v becomes of the order of 1, so we should take into account the shrinking of the Peierls-state volume. So, instead of Eq. (2) we obtain $v = v_0 \tau f(1-v)$, or

$$v = \frac{v_0 \tau f}{1 + v_0 \tau f}. \tag{3}$$

This relation, the principal one for our model, gives growth of v from 0 to 1 with increasing T. The growth has the form of a step centered at $T = W/\ln(v_0 \tau f_a)$, at which $v = 1/2$. The step is smeared out by $\approx T_P^2/W$ (or $1/W$ in the $1/T$ scale). Extrapolation of the LGS description above T_P gives a way to treat the entire PT. Within this approach the transition consists in the LGS-induced destruction of the CDW state.

Let us compare the resulting relation (3) with the experiment. We shall refer mostly to TaS_3—a typical CDW compound, which is among the widely studied quasi-1D conductors.[15] The large ratio $2\Delta/T_P$ for TaS_3, as well as highly anisotropic structure (the anisotropy of conductivity is about 100 at room temperature), argue for the strong fluctuations of the CDW order parameter.

We are beginning with the temperature dependence of resistance, the most common curve characterizing the PT. Within the present model we should calculate the resistance

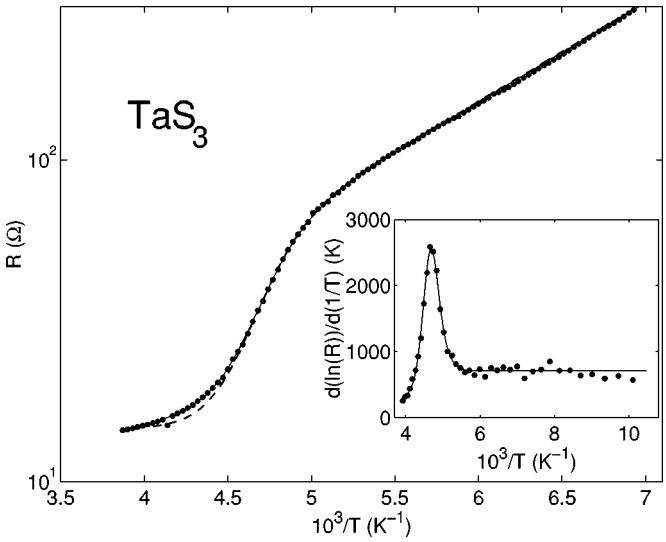

FIG. 1. Fits of a typical $R(T)$ curve for TaS[3] (points) with Eq. (4); for the solid line $W=6600$ K, $v_0\tau f_a=3\times10^{13}$, and $\Delta=710$ K. The broken line shows a similar fit with $B=0$. The inset shows the corresponding logarithmic derivatives.

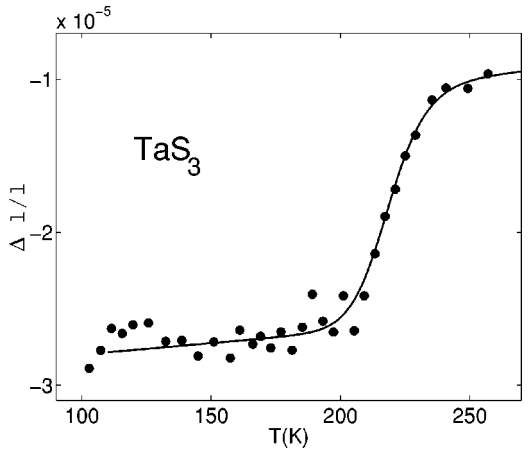

FIG. 2. $\delta l/l$ vs T for a TaS_3 sample. The background approximated with a second-order polynomial is subtracted. The solid line gives a fit with Eq. (3) with $W=6500$ K.

of a mixture of two phases with different resistivities, ρ_c and ρ_n. We shall consider the Peierls-state resistivity $\rho_c \propto \exp(\Delta/T)$, and the normal state resistivity $\rho_n=A+BT$, where A and B are constants. To calculate the resulting resistivity one should consider a complex electric connection of the domains of each phase. For simplicity, we take the contribution of each phase to the resistivity to be just proportional to the volume fraction of the phase, as if for connection in series:[16]

$$\rho = v\rho_n + (1-v)\rho_c. \tag{4}$$

Note that the fluctuations are known to contribute to the conductivity of the Peierls phase due to thermal depinning of the CDW.[14,17,18] According to the model[14] this contribution is governed by the LGS as well and grows as $\exp(-W/T)$. Here we shall not distinguish it from that of the normal phase.

Figure 1 presents an example of a fit of the $R(T)$ curve for TaS_3 with Eq. (4). The fitting is splendid, but one should note that we have taken $B<0$, which is unreasonable for a metal. Even if we take $B=0$, i.e. $\rho_n=$const, the fitting above T_P becomes considerably worse (see the broken line). Below we shall introduce a modification of the model above T_P explaining the slower drop of the CDW fluctuations.

Let us now probe the model for the values which commonly characterize thermodynamic transitions, such as thermal expansion (TE), Young modulus (Y), and specific heat c_p (see, e.g., Ref. 5).

To perform TE measurements, we have developed an interferometric technique for measurements of needlelike samples.[19,20] Figure 2 gives the temperature dependence of the relative length change $\delta l/l$ for TaS_3 in the vicinity of the PT. To exclude the contribution of length hysteresis,[19] we present the half sum of the results obtained upon heating and cooling the sample. A similar curve results if we apply electric field exceeding E_T to remove metastability each time before measuring l. Evidently, the curve presented is close to equilibrium. For all our measurements cooling below T_P results in a *drop* of length by about 10^{-5}. This result is quantitatively similar to that obtained for $K_{0.3}MoO_3$ in the in-chain direction.[21]

TE at the PT has been discussed in Ref. 21. For example, it could be understood within the anharmonic model, taking into account the anharmonic effect of the lattice distortion associated with the CDW. Without going into details, we just assume that the length increase with heating is proportional to the fraction of the normal phase. Thus, the $l(T)$ step should be described by Eq. (3). The fit with $W=6500$ K is quite nice (Fig. 2, the solid line).

As another example we consider the Young modulus temperature dependence, $Y(T)$. One can expect a drop of Y due to the same anharmonic effects. So, with $T\to T_P$ from above one can expect a decrease of Y proportional to the fraction of the CDW volume. However, this is not the whole effect.

Let us recall that depinning of the CDW below T_P reduces the Young modulus.[4,22,23] (This effect is associated with fast relaxation of the CDW deformations which in the pinned state contribute to Y.[23]) As we mentioned above, with increasing T, the fluctuations result in the spontaneous depinning of the CDW,[14,17,18] the concentration of the depinned state growing as $\exp(-W/T)$,[14] which results in the drop of Y with approaching T_P from below. Thus, a dip of $Y(T)$ is expected at T_P.[24] The value of the depinning drop of Y depends on the particular compound. Being anomalously strong for TaS_3,[22] it is not observed for the blue bronze, $\delta Y/Y<5\times10^{-5}$.[25,26] Thus, the dip in $Y(T)$ at $T\to T_P-0$ should be large for TaS_3, and much weaker, if any, for the blue bronze. This expectation agrees with the experiment: inset to Fig. 3 shows $Y(T)$ for TaS_3 from Ref. 6. Large drop of Y is seen with T approaching T_P both from above and from below, whereas only a small dip of $Y(T)$ at $T\to T_P$ from below is observed for the blue bronze in the in-chain direction.[4,5]

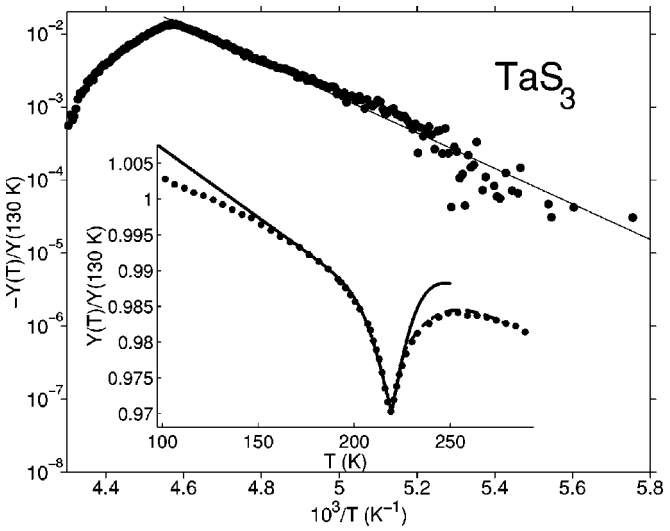

FIG. 3. Arrhenius plot of $-Y(T)$ (a linear function of T is subtracted). The slope of the solid line corresponds to $W=5600$ K. The inset shows the fit of the whole $Y(T)$ curve (the gray circles present only 1/15 of the total experimental points for clarity). The broken line takes into account that for high $v(T>T_P)$ $1-v\propto\exp(-W/2T)$. The data are taken from Ref. 6.

Figure 3 shows the dependence $\delta Y(T)$ below T_P in the Arrhenius axes [a linear dependence $Y(T)$ is subtracted]. The slope of the solid line gives the activation energy 5600 K, giving a good fit nearly up to T_P. To fit the whole $Y(T)$ curve we present Y as $vY_n+v_pY_p+v_rY_r$, where the indices n, p, and r refer to the normal, pinned, and relaxed states respectively $(v+v_p+v_r=1)$. The drop of Y in comparison with the normal state can be presented as $\delta Y=(Y_r-Y_n)v_r+(Y_p-Y_n)v_p$, where $v_r=(1-v)\min[f_r\exp(-W/T),1]$, and $v_p=(1-v-v_r)$. The inset to Fig. 3 shows the fit with $W=6000$ K, $f_r=7.8\times10^{11}$, $v_0\tau f_a=6\times10^{11}$, $(Y_r-Y_n)=0.044$, and $(Y_r-Y_p)=0.011$ in the normalized units. The fit is quite nice, but above T_P the fluctuations fall down slower than the fit gives, as it could be expected (recall also Fig. 1).

It is clear from the examples above that the PT consists in a gradual switching to the state as if having higher free energy, and thus looks as a smeared-out first-order transition. The common check for the first-order transition is the latent heat. Because of the smearing out one can expect a maximum of specific heat c_p. A cusplike feature is clearly seen on the $c_p(T)$ curve for the blue bronze.[5] Recently, a similar feature has been observed also for TaS_3.[8] Being very faint, it was detected as a zigzag pattern on the derivative dc_p/dT. Figure 4 presents the data from Ref. 8 together with d^2v/dT^2, Eq. (3) (the background change of c_p is approximated with a straight line). It is clear that the form of the feature is at least approximately described by our model. Other words, the CDW formation is accompanied by a smeared out step of latent heat whose width is of the order of T_P^2/W. Note that the values of the latent heat $Q\approx0.25RK=5\times10^4$ J/m^3 (Ref. 8; R is the universal gas constant) and the length change $\delta l/l=10^{-5}$ appear to be consistent with the Clausius-Clapeyron equation $dT_p/d\sigma=-T_p(\delta l/l)/Q$ if one takes $dTp/d\sigma\sim1$ K/kbar (Refs. 6 and 15) (σ is the stress along the chains).[27]

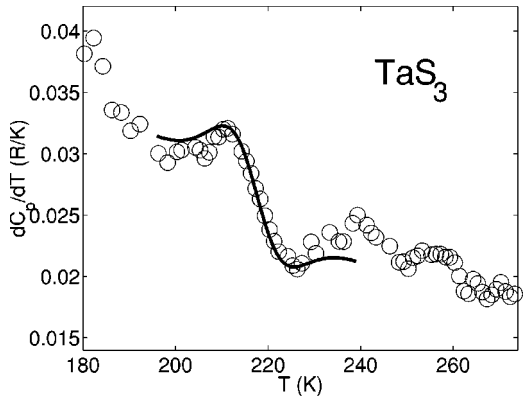

FIG. 4. The temperature derivative of the specific heat of TaS_3. The fit is given by d^2v/dT^2 [Eq. (3)] with $W=10\,000$ K. The data are taken from Ref. 8.

Above T_P one should bear in mind the small sizes of the remnant CDW volumes v_c. As soon as they shrink down below v_0, Eq. (2) is no longer valid, because the new normal volume due to the LGS cannot exceed v_c. With simple assumptions at high enough T one can obtain $(1-v)\propto\exp(-W/2T)$; the appropriate fit for $Y(T)$ is given with a broken line in the inset to Fig. 3. This consideration also explains the behavior of the $R(T)$ curve above T_P (Fig. 1).

Thus, the LGS model fairly describes the temperature evolution of the principal parameters in the vicinity of the PT. All the fits proposed have transparent physical sense. The main parameter of the model—the energy W—is close to the values for the barrier characterizing thermally initiated PS.[12–14] Evidently, LGS is governed by the same process as PS. (Some indications of the connection between PS and the PT have been given in the early works.[10,11,14,28]) So, it would be natural to consider excitation of dislocation loops[29] as a precursor effect below T_P. Excitation of the dislocation loops is being considered as a possible origin of softening of solids[30] or similar transitions in liquid helium and HTSC's.[31] This approach gives critical expansion and proliferation of the loops due to their mutual screening. The apparent absence of the critical behavior in our case could mean that the CDW excitations practically do not interact up to T_P. Note that while for a conventional crystal the smallest possible radius of a dislocation loop is of the order of the lattice constant, for the CDW it is of the order of $\xi_\perp$. Such an object (i.e., an amplitude soliton) covers a volume $\sim\xi^3\equiv\xi_\parallel\xi_\perp^2$, where $\xi_\parallel$ and $\xi_\perp$ are the in-chain and the transverse amplitude correlation lengths, respectively; the soliton can perturb a still higher volume, where, say, the conductivity is increased. Thus, the condition $v=1/2$ can be achieved when the concentration of the excitations is still much less than $1/\lambda s$, where λ is the CDW wavelength and s is the area per chain.

The concentration of the solitons could be estimated as $(1/\lambda s)\exp(-W/T)$, where W is the energy of such an excitation. Then, $v\sim(\xi^3/\lambda s)\exp(-W/T)$. At $T=T_P$ we have $(\xi^3/\lambda^3)\exp(-W/T)\approx1$, and come to the estimate

$$T_P \simeq \frac{W}{\ln(\xi^3/\lambda s)}. \quad (5)$$

With $\xi^3/\lambda s = 10^3$ we obtain $T_P = W/7$, which can give an idea of the low value of T_P in comparison with W. A higher ratio W/T_P might be obtained if we take into consideration the large wavelengths of the fluctuations of the CDW stress along the chains. According to Ref. 9 they can considerably exceed $\xi_\parallel$ and, consequently, the LGS volumes could appear much larger than ξ^3.

According to our estimates, the excitations would begin to turn into dislocation loops only above T_P. So, within the model, the metallic state develops at lower temperature than the critical behavior is expected to begin. As far as we comprehend, the approach proposes a different type of phase transition, which does not comprise T_P as a parameter. At the same time, the PT in a sense resembles a first-order transition. The model successfully works both below and above T_P, though further extrapolation of the approach to higher temperatures requires further development of the model. The underlying microscopic mechanisms of the LGS also need deeper understanding. Though the model requires further grounds it gives a limpid insight into the processes inside the CDW near T_P.

We are thankful to J. W. Brill, G. Mozurkewich, and D. Starešinić for granting the experimental results at our disposal, to V. V. Frolov and R. E. Thorne for furnishing the samples, to V. I. Anisimkin, L. Burakovsky, S. N. Artemenko and, again, to J. W. Brill for helpful discussions. This work has been supported by the RFBR (Grant Nos. 04-02-16509 and 02-02-17301), Jumelage (CNRS and RFBR, No. 03-02-22001), INTAS (Grant No. 01-0474), and by the State programme "Physics of Solid-State Nanostructures" (No. 40.012.1.111.46).

*Electronic address: pok@cplire.ru

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