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Evidence for one-half charge-density-wave wavelength pinning periodicity in Peierls conductors

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It is shown that, for transition-metal trichalcogenides $NbSe_3$, for TaS_3 both with a monoclinic and an orthorhombic unit cell, and for transition-metal tetrachalcogenide $(TaSe_4)_2I$, compounds which exhibit transport properties associated with charge-density-wave motion, the linear relationship between the current carried by the charge-density wave and the fundamental frequency of the ac voltage detected in the nonlinear state leads to a pinning potential periodicity which is half the charge-density-wave wavelength in agreement with the recent theory of Josephson oscillations of Barnes and Zawadowski.

After $NbSe_3$,[1] nonlinear transport properties measured at temperatures below a Peierls transition have been measured in many other compounds such as TaS_3 both with the orthorhombic[2,3] and monoclinic[3] unit cell, in NbS_3,[4,5] in blue bronze $K_{0.30}MoO_3$,[6] and very recently in a transition-metal tetrachalcogenide $(TaSe_4)_2I$.[7] The extra conductivity observed was explained by a current-carrying charge-density-wave (CDW) state as proposed by Fröhlich[8] in 1954. The translation invariance of the phase of the CDW in real systems is broken by commensurability pinning or impurity pinning.[9] A finite electric field must be applied in order to dislodge the CDW from the pinning centers.[10] Above this threshold electric field, a periodic signal is measured through the voltage leads of the sample.[11] This ac signal was interpreted as the motion of the CDW in the anharmonic periodic pinning potential created by the impurities.[12] As all the lattice distortions of the compounds exhibiting CDW depinning were weakly incommensurate with the lattice, it was supposed that the pinning periodicity was the CDW wavelength. However, if the CDW is commensurate, the pinning periodicity would be the lattice constant along the chains.[13]

Very recently, Barnes and Zawadowski[14] studied the interaction of a moving CDW with impurities. They show that the CDW can be considered as the superposition of two macroscopic quantum states which are split by the motion of the CDW. Each state is composed of electron-hole pairs with, respectively, total momentum $\pm Q$. A second-order perturbation theory takes into account two impurity scatterings which transfer an electron-hole pair with momentum Q to an electron-hole pair with momentum $-Q$. The result is an energy density periodic in space with a periodicity $\lambda_{CDW}/2$. The first-order perturbation theory leads to an energy density also periodic in space with the periodicity λ_{CDW} as assumed in classical models.[12,15]

If in $\vec{k}$ space the Fermi distribution moves at the velocity v, the current in the sample is

$$J_{CDW} = ne v \quad , \tag{1}$$

where ne is the total electron concentration in the bands affected by the CDW. The CDW velocity can be written as the product of the fundamental frequency measured in the ac voltage and the pinning periodicity. Therefore

$$J_{CDW}/\nu = ne \lambda_{pinning} \quad ;$$

ne can be calculated by simple band calculations: the Fermi level is at $q = 2k_F = 2\pi/\lambda_{CDW}$ and, in absence of any Peierls transition, there are two electrons in the band filled up to $b^* = 2\pi/b$, where b is the unit-cell parameter along the chain axis. Also,

$$ne = p \frac{2b}{\lambda_{CDW}} \frac{1}{v_{\text{unit cell}}} \quad ,$$

where p is the number of bands affected by the CDW and $v_{\text{unit cell}}$ the volume of the unit cell. Consequently,

$$\frac{J_{CDW}}{\nu} = \frac{2ep}{\mathcal{A}} \frac{\lambda_{pinning}}{\lambda_{CDW}} \quad , \tag{2}$$

with $\mathcal{A}$ the cross section of the unit cell.

J_{CDW} is obtained directly by measuring the nonlinear characteristics $V(I)$, and under the assumption that

$$J_{CDW} = J \left(1 - \frac{R}{R_n} \right) \quad , \tag{3}$$

with J the applied current density, R the resistance for this J value, and R_n the Ohmic resistance in the linear state below the threshold field. The fundamental frequency ν is measured as a function of J by Fourier analysis of the noise voltage across the sample. The fundamental frequency is the first frequency which appears in the Fourier-transformed voltage near the threshold.

The linear relationship between J_{CDW} and ν is very well established and temperature independent for any sample studied for temperatures well below the Peierls transition temperature where the CDW gap is well developed.[1-3,7] For $NbSe_3$ it was reported recently that J_{CDW}/ν decreases to zero at the Peierls transition T_2,[16] in agreement with a BCS expression for the temperature dependence of the order parameter. However, for the samples we have studied, we find that, in the vicinity of the Peierls transitions, J_{CDW} does not vary linearly with ν, which might indicate the failure of expression (3) for calculating J_{CDW}: for small J_{CDW}, the variation of ν is more pronounced than for higher J_{CDW}, but for current densities in the order of 100 A/cm^2, the slope between J_{CDW} and ν is identical with that measured at low temperatures for any J_{CDW}. Therefore considerations that we present hereafter concern only the low-temperature limit. In Fig. 1, we have plotted J_{CDW} as a function of ν for the samples exhibiting CDW transport [$NbSe_3$, both TaS_3, $(TaSe_4)_2I$]. The cross section of the samples taken for the calculation of J_{CDW} is deduced from the value of the resistivity measured on samples of the same batch. The values of the resistivity listed in Table I are an average of several crystals whose cross section has been measured with a scan-

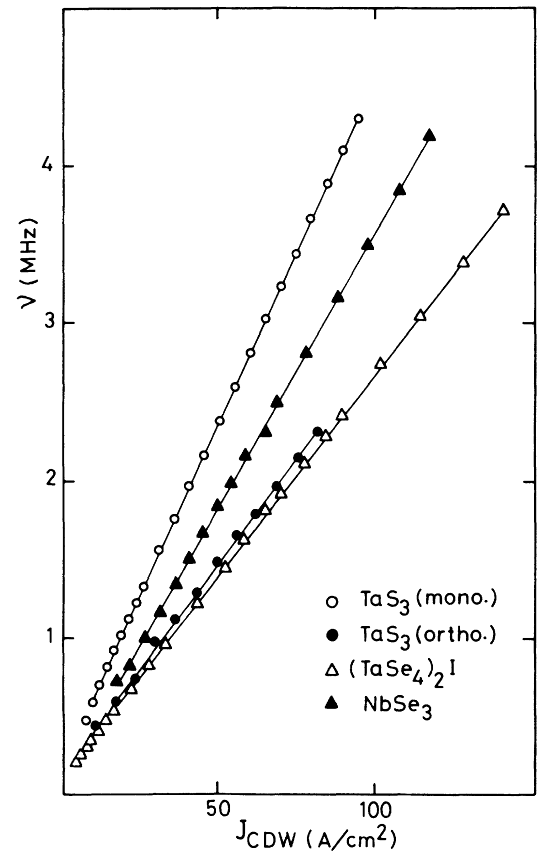

FIG. 1. Variation of the fundamental frequency ν measured by the Fourier-transformed voltage as a function of the current carried by the CDW at a low temperature compared with the Peierls transition temperature for the transition-metal tri- and tetrachalcogenides exhibiting CDW transport (measurements at $T=110$ K for TaS$_3$ monoclinic, $T=45$ K for NbSe$_3$, $T=81$ K for TaS$_3$ orthorhombic, and $T=150$ K for (TaSe$_4$)$_2$I.

ning electron microscope. The experimental values of J_{CDW}/ν are listed in Table I. The measurements on NbSe$_3$ performed on a crystal with a resistance ratio between room temperature and helium temperature of 160 are in agreement with results reported before.[1]

In Table I, we have also estimated the number of bands affected by each CDW. Monoclinic NbSe$_3$ and TaS$_3$ undergo two independent CDW's, respectively, at $T_1=145$ K and $T_2=59$ K for NbSe$_3$ (Ref. 1) and $T_1=240$ K and $T_2=160$ K for TaS$_3$.[3] Their structures are similar and six chains form the monoclinic unit cell. As for any trichalcogenide, their electronic properties are governed by the strength of the chalcogen-chalcogen bond. Following Wilson[17] and band calculations,[18,19] two chains are involved with each CDW. Recent NMR measurements on NbSe$_3$ (Ref. 20) show very well the three different niobium sites and the successive influence of the two Peierls transitions on two niobium sites. The structure of TaS$_3$ with the orthorhombic symmetry is unknown but there are 24 chains in the unit cell. X-ray photoemission spectroscopy measurements reveal that the Ta 4f signal can be fitted by two entities tantalum 4 and tantalum 5 in the ratio 1:1. Also, sulfur is found in two oxidation states S^{2-} and $S_2{}^{2-}$ in a ratio of approximately 1:1.[21] These results lead us to suppose that there are two types of tantalum atoms with perhaps different coordination or, more likely and similarly with NbSe$_3$, different trigonal prismatic chains with various S-S lengths. In this case, the CDW would affect half the number of chains of the unit cell. TaS$_3$ undergoes a Peierls transition at $T_0=215$ K. Recently we reported that the component of the distortion along the chains was incommensurate and locks to the commensurate value of 0.25 at $T_0'=140$ K.[22] Below T_0' the distortion wave vector is $\frac{1}{2}a^*$, $\frac{1}{8}b^*$, $\frac{1}{4}c^*$. This incommensurate-commensurate locking of the component along the chains induces anomalies in linear and nonlinear transport properties but does not imply a commensurability pinning: because of the eight unit cells in the transverse orientation along b, to find the same phase and the pinning potential in $V_0\cos4\phi$, the phases of the CDW on adjacent unit cells are not in a commensurability configuration. (TaSe$_4$)$_2$I has the simplest structure: there is a unique type of chain but, because of the iodine configuration, the unit cell is described with two chains.[23]

With these numbers and without adjustable parameters we find that for all the compounds $\lambda_{pinning}/\lambda_{CDW}$ is nearly 0.5. The slight discrepancy for NbSe$_3$ might come from the partial condensation of electrons below the Peierls transitions, the ground state remaining metallic. Very small electron pockets at helium temperature have been detected by Shunikov-de Haas oscillations.[24]

In fact, the two periodicities in $\lambda_{CDW}/2$ and λ_{CDW} are present and it remains for us to study theoretically and experimentally their mutual strength as a function of the pin-

TABLE I. Parameters and experimental data for the determination of $\lambda_{pinning}/\lambda_{CDW}$ following expression (2). J/ν are deduced from Fig. 1 and p is the estimated number of bands affected by each CDW.

	Structure	Peierls transition temperature (K)	Section of the unit cell (Å^2)	ρ ($\mu\Omega$ cm)	J/ν A/MHz cm^2	p	$\frac{\lambda_{pinning}}{\lambda_{CDW}}$
NbSe$_3$	Monoclinic[a]	145[b]	147.48	300 ±20	25[b]	2	0.575
		59			25	2	0.575
TaS$_3$	Orthorhombic[c]	210[d]	558.43	320 ±20	38[e]	12	0.55
TaS$_3$	Monoclinic[f]	240[e]	133.33	410 ±20	20[e]	2	0.42
		160			20	2	0.42
(TaSe$_4$)$_2$I	Tetragonal[g]	262.5[h]	90.84	1500 ±200	38[h]	2	0.54

[a] Reference 25.
[b] Reference 1.
[c] Reference 26.
[d] Reference 28.
[e] Reference 3.
[f] Reference 27.
[g] Reference 23.
[h] Reference 7.

ning and of the temperature. The observation, in some cases, of subharmonics at $\nu/2$ with a small amplitude might be the evidence of the λ_{CDW} periodicity. But in the crystals studied up to now the $\lambda_{\mathrm{CDW}}/2$ periodicity, as predicted by Barnes and Zawadowski,[14] seems to be the predominant phenomenon.

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