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Neutron study of the Peierls transition and low-frequency excitations in $(\text{TaSe}_4)_2\text{I}$

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Neutron scattering results on the lattice dynamics and Peierls phase transition of $(\text{TaSe}_4)_2\text{I}$ are presented. The room temperature phonon dispersion curves reflect the stiffness of the $(\text{TaSe}_4)_\infty$ chains and the comparatively weak transverse interchain interactions. The response of the [110] polarised TA mode, connected with the Peierls instability, is found to be weakly temperature-dependent. Correlation lengths associated with the diverging "central peak" are determined and are found to be nearly isotropic. We discuss the significance of these results from the point of view of electron-phonon theory and stress the importance of allowing for the interaction between optic and elastic degrees of freedom.

STRUCTURE OF $(\text{TaSe}_4)_2\text{I}$

$(\text{TaSe}_4)_2\text{I}$ belongs to the family of transition metal tetraselenides[1] of general formula $(\text{MSe}_4)_n\text{I}$ with $\text{M}=\text{Ta}, \text{Nb}$ and $n=2, 3, 10/3$, the crystal structure of which consists in an arrangement of strongly bonded $(\text{MSe}_4)_\infty$ chains parallel to the tetragonal c-axis. In each chain, M atoms and Se_4 rectangles alternate, the shortest intrachain Se-Se distance corresponding to a Se_2^{2-} dimer.

Band structure calculations [2] suggest a single d_z^2 electronic band at the Fermi level. For $(\text{TaSe}_4)_2\text{I}$ this band is 1/4-filled with one free electron per $(\text{Ta}^{4+} \text{ Ta}^{5+} 4\text{Se}_2^{2-} \text{ I}^-)$ formula unit. Consecutive Ta atoms occupy two alternating non-equivalent sites, but the Ta-Ta distance is unique ($d_{\text{Ta-Ta}}=3.206 \text{ \AA}$). Due to the Se_4 -unit rotation pattern, the crystallographic unit cell parameter is $c = 4d_{\text{Ta-Ta}}$

On that basis, one may expect the compound to be an insulator because the Fermi wavevector corresponds to a Brillouin zone boundary:

$$k_f = 1/4(\pi/d_{\text{Ta-Ta}}) = \pi/c = c^*/2$$

However Gressier et al..[2] have argued that, due to the screw-symmetry of the undistorted chain, there is no energy gap associated with the $c^*/2$ zone

boundary. In addition, k_f in the 3D solid may deviate slightly from the commensurate value $c^*/2$ due to interchain interactions

PEIERLS TRANSITION

The lowering of the conduction band energy by opening of a Peierls gap has also been discussed. The periodic lattice distortion which Gressier et al. [2] have considered is a Ta-tetramerisation along the chain (or something closely similar, when k_f is not exactly at $c^*/2$). They show that in the case of a $1/4$ -filled d_z^2 band the energy gain is small and that this is probably the reason why the undistorted structure is observed to be stable for $T > 260$ K. In contrast, compounds with $1/2$ -filled or $1/3$ -filled d_z^2 bands, such as VS_4 or $(\text{NbSe}_4)_3\text{I}$ are stable only in the semi-conducting distorted state.

SATELLITE REFLECTIONS

In $(\text{TaSe}_4)_2\text{I}$ below 260 K new satellite reflections are observed and the electrical response shows non-linear effects characteristic of a CDW-groundstate.

The wavevector of the associated lattice distortion is small, viz. $q_s = (\pm\eta, \pm\eta, \pm\delta)$, with $\eta = 0.045$ and $\delta = 0.085$, which means that satellite reflections ($T < T_P$) are located close to fundamental Bragg peaks (cf. Fig. 1 below).

Fig. 1: Reciprocal space sketch of satellite peak positions near a (hhl)-type fundamental Bragg peak (closed circle). The shaded plane corresponds to the (hhl) scattering zone. The polarisation of the modulated atomic displacements is such that the in-plane satellite reflections are nearly extinct (open squares)

This low value of q_s can be understood on the basis of the above-mentioned band structure arguments, with the additional assumption of antiphase CDW ordering on adjacent chains.

What is not understood from simple electron-phonon coupling arguments is the fact that the satellite intensity selection rules, as pointed out by Fujishita et al. [3] and Lee et al. [4], are consistent with atomic displacements of the transverse acoustic type polarised in the basal plane, in contrast to the expected c-polarised (-Ta-Ta-) tetramerisation mode

CORRELATION LENGTHS

There are other unusual features associated with the Peierls instability in $(\text{TaSe}_4)_2\text{I}$, notably the very small anisotropy of the correlation lengths, parallel and normal to the chains. Inelastic neutron scattering data (see below) show that, as $T \rightarrow T_p$, the main temperature-dependent precursor effect is the growth of a central component whose energy width is resolution limited (<10 GHz). The corresponding inverse correlation lengths, as obtained from cold-neutron elastic 3-axis data, are shown in Fig. 2 below.

Fig. 2: Temperature dependence of the Lorentzian halfwidths of the critical scattering around $(2-\eta, 2+\eta, 4+\delta)$. After Ref. [5].

Contrary to expectations, the in-chain ($//c^*$) and in-plane ($//a^*\pm b^*$) correlation lengths are of comparable magnitude. Similar (i.e. nearly isotropic) correlations have been reported by Fujishita et al. [6], using x-ray scattering, on the isomorphous compound $(\text{NbSe}_4)_2\text{I}$.

LATTICE DYNAMICS

The room temperature phonon dispersion curves have been investigated in the main symmetry directions and at low frequencies, by inelastic neutron scattering. The results, shown in Fig. 3, extend previous measurements in Ref. [7].

Fig. 3: Phonon dispersion curves in $(\text{TaSe}_4)_2\text{I}$ at room temperature (after Ref.[5]). Modes polarised along the chains (normal to the chains) are shown as closed (open) symbols. The sound velocities (solid lines) are taken from Ref. [8]. .

The two outstanding features in the dispersion curves shown in Fig. 3 are:

- the upward curvature of TA-mode along (00ξ) , characteristic of a large chain-bending stiffness
- the flat low-lying (0.2-0.3 THz) TA_z branches, polarised along the chains and propagating in the basal plane indicating weak transverse interchain interactions.

We suggest that the C_p/T^3 anomaly at 1.8 K in $(\text{TaSe}_4)_2\text{I}$, is due to the excess low-frequency density of states arising from the flat TA_z branches. This hypothesis is supported by direct neutron time-of-flight measurements of the phonon density of states [9].

SOFT MODES

In the neighbourhood of the satellite position, labeled here $q_s=(\eta,-\eta,\delta)$, we study the inelastic response from the TA mode polarised along $[110]$, whose eigenvectors are related to the frozen modulated displacements below T_p . As shown in Fig. 4a, some limited softening is seen as $T \rightarrow T_p$, as well as an increase in phonon damping. No decoupling between phase and amplitude modes is observed for $T < T_p$, where the response can still be fitted with a single oscillator response (Fig. 4b).

Fig. 4. (a) Constant-Q spectrum at the satellite position (A-point in Fig. 1) above and below T_p ; (b) Single oscillator fit: temperature dependence of mode frequency and damping. After Ref. [5].

CONCLUSION

The softening of the acoustic phonon whose polarisation vector is related to the periodic modulation below T_P , does not have a critical character. Critical behaviour is observed on the elastic (or unresolved quasielastic) central peak whose intensity and correlation lengths diverge on approaching T_P . This and the absence of decoupling between phase and amplitude modes below T_P , lead us to place the phase transition in $(TaSe_4)_2I$ in the order-disorder class. The existence of Peierls transitions with order-disorder dynamics has been predicted by Aubry et al. [10], in the context of strong coupling theory (bipolaronic CDW's). The large value of the low-temperature Peierls gap ($2\Delta=11.4k_B T_P$ in $(TaSe_4)_2I$) together with the apparent absence of a 1-D fluctuation regime above T_P , is certainly consistent with the bipolaronic picture.

The transverse acoustic character of the distortion observed below T_P , is in sharp contrast with the Ta-tetramerisation mode expected from simple electron-phonon theory. This illustrates the need to properly account for the interaction between the electronically-coupled optic variables and the crystalline elastic degrees of freedom. This interaction is essential in the case of $(TaSe_4)_2I$, as the periodicity of the Peierls instability is very close to the periodicity of the undistorted lattice ($2k_F \approx c^*$).

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