Anomalous features of the CDW transition in metallic 2H dichalcogenides

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ABSTRACT: *The metallic dichalcogenides of transition metals which crystallise in the trigonal prismatic 2H structure, are considered as a model family for the study of charge-density-wave transitions of the metal-metal type. We review different properties and their evolution in the series: transport, specific heat, magnetic susceptibility, soft phonon dynamics. For temperatures higher than the transition temperature, T_d , many characters underline the departure from the normal metal behaviour as well as from the behaviour resulting from the presence of the simple soft mode predicted by weak-coupling theories. A phenomenological analysis rather suggests for this family a very strong coupling mechanism involving local vibronic pseudo spins, narrow-band character and proximity to an order-disorder transition.*

1.Introduction.

Metallic dichalcogenides of transition metals, MX_2 ($\text{M}=\text{Nb}, \text{Ta}$; $\text{X}=\text{S}, \text{Se}$), which crystallise in the trigonal prismatic 2H lamellar structure are well-known for undergoing charge-density-wave (CDW) transitions linked to their two-dimensional character [1-3]. The CDW transition temperatures, T_d , are 123 K, 80 K and 33 K for TaSe_2 , TaS_2 and NbSe_2 , respectively, while NbS_2 undergoes no phase transition. The accompanying incommensurate lattice distortion which also develops below T_d is however close to the commensurate modulation wave-vector $\mathbf{Q}=(a^*/3, 0, 0)$. The modulation is indeed triple-Q and the displacements of ionic centres belong to the Σ_1 symmetry (this predominantly consists in a longitudinal motion of the cations). The preceding characters are shared by all the compounds undergoing the CDW transformation. Continuous efforts in structural studies over many years revealed also a variety of additional features [4,5] which confirm the intimate similarities existing between these compounds.

The mechanism of the transition is thought to mainly result from the electron-phonon interaction in presence of quasi-2D "nesting" conditions. The different band structure calculations [6] for these systems agree about a Fermi Surface made of quasi-cylindrical pockets, the first ones elongated along HKH edges and the last one with its axis along $\Gamma\Gamma\Gamma$ in the Brillouin zone. A van Hove anomaly resulting from the connection between the zone centre isoenergy surfaces and the edges ones is also possible but its distance from the Fermi level, ϵ_F , is still uncertain. The total width of the predominantly d_{z^2} character band near ϵ_F is more than 2eV. A detailed theoretical investigation of the electron-phonon interaction in those systems was carried out by MOTIZUKI and co-workers [7] on the basis of an effective tight binding model. This study shows the importance of both the nesting conditions and of the q-dependent

electron-phonon coupling coefficient for causing the lattice instability. This approach, a weak coupling one in essence, obtained good success in particular by predicting the right symmetry for the soft phonon mode. However it failed to provide a satisfactory evaluation of the different observed T_d 's. This can be due to limits in the calculation but most probably results from more basic reasons involving the need for a short coherence length model [8] and a strong coupling approach [9]. The strong coupling nature of the present CDW's received renewed support recently owing to the use of STM spectroscopy which indicates very large ratios between the CDW gap and T_d : $2\Delta/kT_d = 15.2, 15.4$ and 23.9 for TaSe_2 , TaS_2 and NbSe_2 , respectively [10]. These values remain however much lower than the I.R. reflectivity data [11]: 46 in the case of TaSe_2 . In the following, we review selected experimental topics which could help for a better understanding of the CDW formation in this model family.

2. Macroscopic properties.

At first sight, transport properties of 2H-MX_2 compounds appear to follow closely the normal metal behaviour. This contrasts with the 1T-polytypes for which case the CDW transition is of the metal-non metal type. In 2H systems both the distorted and the undistorted phase, above and below T_d , are fully metallic. At lower temperatures, the resistivity $\rho(T)$ behaves like T^3 or T^5 for Nb and Ta compounds respectively, as expected for d metals [12]. For distorted systems, but not in NbS_2 , a large positive magneto resistance is observed below T_d which is due to magnetic breakdown effects in the reconstructed band structure [13]. Near T_d , a small anomaly can be detected in $\rho(T)$ as a result of the CDW pseudo-gap formation which is confirmed by the strong increase in the absolute value of the Hall coefficient, R_H [12]. Above T_d however, several difficulties raise in comparison with the above normal aspects. The first problem concerns the resistivity of TaSe_2 and, to a less extent of TaS_2 , for which an additional constant contribution is present above T_d . The presence of a correlated minimum in the phonon dominated thermal conductivity is strongly suggestive of a pseudo-spin mechanism for scattering both electrons and phonons [14]. Transport experiments can be then accounted for by an additional constant relaxation rate which is progressively reduced as the CDW order sets in below T_d . The analysis of the specific heat supports the proposed scheme which basically represents the CDW transition as an order-disorder one [14,15]. The form of the specific heat anomaly near T_d in TaSe_2 is well accounted for by a jump contribution plus a gaussian fluctuation one reflecting the short coherence length ($\xi_0 \sim 10\text{\AA}$) [16]. This was considered by McMILLAN as an argument in favour of a "local soft mode" [8]. Our approach goes one step further by considering the order-disorder character of the transition which agrees well with the variation of the transition entropy $\Delta S \propto R \ln 2$, once one refers to the unit cell of the distorted phase i.e. nine times that of the high temperature crystallographic phase. This view implies that the local soft mode has not a continuous character but it is rather of a pseudo-spin nature with a double degeneracy. A detailed picture of the atomic displacements and of the accompanying CDW modulation was proposed [14].

However, the above picture breaks down for the other compounds in the series. First, the transition entropy becomes significantly less than the order-disorder value. Instead, it scales with the transition temperature [15]. Secondly, a refined investigation of $\rho(T)$ shows the existence of "saturation" effects, i.e. a negative curvature, occurring in the higher temperature range. This effect is most pronounced for NbS_2 . This behaviour is not fortuitous as shown by the thermoelectric power, S [15]. The latter has negative values at room temperature for all compounds. This contradicts the positive Hall effect and the exclusively positive charge carriers predicted by band calculation. In addition, large absolute values are achieved

TABLE I

	NbS ₂	NbSe ₂	TaS ₂	TaSe ₂
2 γ (in K)	570	770	820	830
$\delta\epsilon_0$ (in K)	75	57	51	13
2 Δ (in K)	-	790	1160	1850

especially for NbS₂ which exceeds 20 μVK^{-1} at room temperature and this is inconsistent with a normal metal behaviour. The contradiction can be overcome by assuming a resonant level structure close to ϵ_F by analogy with the case of mixed-valence systems. Then, the S-vs-T curves above T_D can be easily fitted and provide a quantitative estimate for the width, 2γ , and for the shift relative to ϵ_F , $\delta\epsilon_0$, of this structure [15]. The corresponding results are shown in TABLE I. These show that, excepting NbSe₂, the widths are of similar magnitude for the other compounds and that differences between them mainly come from differences in position relatively to the Fermi level. We also note that this phenomenological treatment is also able to explain consistently the excess departure of the Wiedeman-Franz ratio from the Lorentz number [15]. Interestingly, this structure is also reflected in the magnetic susceptibility which shows a departure from the usual Pauli paramagnetism. In Figure 1, the normalised curves for the different compounds nearly coincide above T_D . In this range, using the first and second derivatives of the density of states, $\nu(\epsilon)$, χ can be expanded as $\chi \propto \nu(\epsilon_F) + 1/6\pi^2(\nu''(\epsilon_F) - \nu^2(\epsilon_F)/\nu(\epsilon_F))(k_B T)^2 \approx \nu(\epsilon_F) + 1/6\pi^2 T^2/T_0^2$. From the data of Figure 1, one obtains $T_0 \sim 700$ K, a value which agrees well with 2γ . In Table I we have also reported the CDW pseudo-gap values obtained from STM [10]. These values are of the order of magnitude of 2γ though generally higher, especially in the case of TaSe₂. This may be due to the way the pseudo-gap is defined in presence of dispersion effects. If confirmed, this relative agreement would suggest that the CDW gap formation is limited by a narrow-band structure near ϵ_F . This could also constitute an issue for explaining why χ does not reduce when crossing T_D contrary to what is observed for Ta-compounds (see Figure 1).

FIGURE 1. Magnetic susceptibility of TaSe₂ (squares), TaS₂ (triangles) and NbSe₂ (circles), normalised at $T=300$ K.

3. Inelastic neutron diffusion.

The above phenomenological approach seems to provide a satisfactory representation of macroscopic quantities. However, it has to be supported by more microscopic evidence. This motivated our reinvestigation of the soft phonon dynamics by measuring inelastic diffusion of neutrons using different diffractometers at ILL and LLB. We are mainly focusing on the study of NbSe₂ and TaSe₂.

MONCTON and co-workers [4] have measured the room temperature dispersion curve of the mode Σ_1 . This possesses a peculiar form with a broad dip centred around $Q=(a^*/3,0,0)$, the position of the over-structure wave-vector in the reciprocal lattice. Our investigations fully confirm this result at a quantitative level. However, the energy scans in the vicinity of Q show that, despite improved resolution conditions, the broad soft phonon oscillator is possibly mixed with an even broader structure. In the case of NbSe₂, we measured the softening of the Q -phonon down to T_d and showed that the latter is complete within experimental accuracy [16]. However, two modes with the Σ_1 symmetry seem present at least in the lower temperature range: ω_1 , the higher energy one and, ω_2 , the lower energy one. Then, analysing the energy scans for all temperatures on the basis of two oscillator contributions, an anomalous temperature dependence is obtained for ω_2 . The latter is roughly constant between 100 K and 300 K, while, below 100 K, it decreases more rapidly than the expected $\omega_2^2 \propto (T - T_d)$ law. ω_1 does not change significantly with temperature but its value is determined with a large uncertainty. Recently, we confirmed the different behaviour of the mode softening which occurs in TaSe₂ [17]. This concerns particularly the presence of a gap at T_d in the $\omega_Q(T)$ curve as first obtained in Ref.[4]. No extra oscillator seems to soften unlike the case of NbSe₂. Instead, a broad contribution is present and is well represented by a lorentzian shape. The confirmation of a gap in the $\omega_Q(T)$ curve, supports the order-disorder mechanism for the transition in TaSe₂ as this behaviour is predicted by theoretical models [18] which, in addition, predict a complex inelastic structure. On the contrary, NbSe₂ looks shifted towards the displacive regime. However, the complex structure still shown by the inelastic response indicates the departure from the purely displacive case. Definite conclusions concerning this point have also to consider the specific features of the 2H structure like interaction of different modes of Σ_1 symmetry or 2D-3D dimensionality crossover.

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