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Temperature dependent phonon dispersion in 2H-$NbSe_2$ investigated using inelastic neutron scattering

K Schmalzl[1,2], D Strauch[3], A Hiess[2] and H Berger[4]

[1] Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany
[2] Institut Laue-Langevin, 38042 Grenoble Cedex 9, France
[3] Institut für Theoretische Physik, Universität Regensburg, 93040 Regensburg, Germany
[4] EPFL, 1015 Lausanne, Switzerland

E-mail: schmalzl@ill.fr

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Abstract

The longitudinal low frequency acoustic and optic phonon modes of 2H-$NbSe_2$ have been determined for the Γ–M direction with inelastic neutron scattering at 50 K close to the charge density wave transition temperature.

We found a softening of the two low frequency modes which are attributed to the same symmetry close to the charge density wavevector. We also found indications that the anomalous frequency seems to soften further for off-symmetry directions.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

2H-$NbSe_2$ belongs to the group of quasi-two-dimensional layered transition metal dichalcogenides. The 2H polytype consists of stacked hexagonal planes with van der Waals bonding between adjacent layers. Due to the almost two-dimensional structure very anisotropic electronic or structure related properties like thermal expansion and sound velocity are found. At low temperatures several interesting electronic properties appear: an incommensurate charge density wave (CDW) instability with a wavevector close to $Q = (a^*/3, 0, 0)$, with $a^* = 4\pi/\sqrt{3}a$, along the Γ–M direction is observed at $T \approx 35$ K. A controversy is still not settled as to whether the CDW instability in the layered dichalcogenides originates from Fermi surface nesting, see e.g. [1–3], or from saddle points in the electronic band structure [4], while from recent *ab initio* calculations [5] both approaches cannot be supported. Superconductivity develops for $T \leqslant 7$ K within this ordered state.

Due to transport anomalies in these systems there is renewed interest in the electron–phonon coupling which is likewise suspected to be anisotropic; see e.g. [6]. Even though the anisotropic behaviour seems to be one of the key properties of the transition metal dichalcogenides, the anisotropy and extent of the anomaly near $Q = (a^*/3, 0, 0)$ have not been investigated in detail except for the extent along the $[\xi 00]$ direction. The behaviour in the perpendicular directions is unknown and can be expected to be different for in-plane and perpendicular directions.

2H-$NbSe_2$ undergoes a phase transition consistent with a second-order behaviour to an incommensurate CDW phase at $T_{CDW} = 35$ K, where no lock-in seems to occur down to a temperature of 5 K [7, 8].

Some of the phonon branches in $[\xi 00]$ and $[00\xi]$ directions have been studied at room temperature in the lower energy region up to 12 meV with INS [7, 8] or inelastic x-ray scattering [9]. A Kohn anomaly is observed in the longitudinal Σ_1 modes at about one third along the $[\xi 00]$ direction close to the CDW wavevector. Since the Σ_1 modes involve longitudinal atomic displacements, they are appropriate for coupling to the CDW. Also similar metal dichalcogenides like 2H-$TaSe_2$ show an anomaly in the Σ_1 phonon mode [8].

The temperature dependence of the longitudinal Σ_1 modes in 2H-$NbSe_2$ has been studied by Ayache *et al* [10] at the specific wavevector $Q = (a^*/3, 0, 0)$. They found a softening of the lower branch (denoted in this work as ω_1) in the temperature range 100–33 K. For the higher frequency mode (ω_2) they claimed to have found no change in the range 300–50 K; however their data at 50 K appear somewhat scarce.

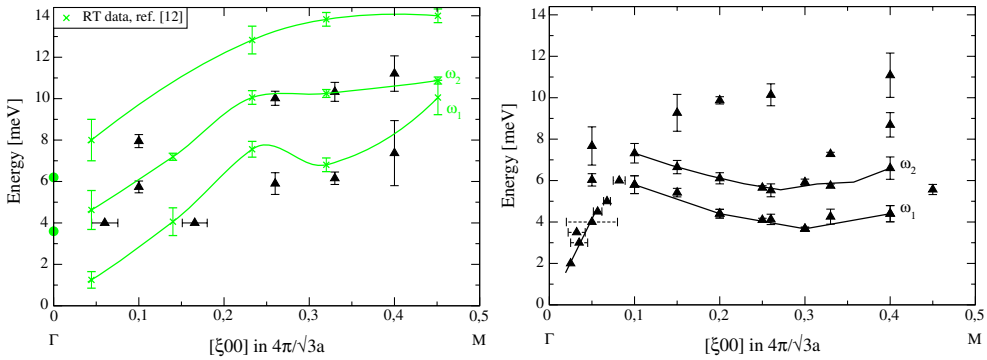

Figure 1. Left panel: selected low energy phonons of 2H-$NbSe_2$ at 200 K in comparison with room temperature data from [9]. The circles at Γ are Raman data at RT from [11, 12]. Right panel: constant energy and constant Q scans of the low energy region at 50 K. The error bars indicate the width of the measured peaks in energy or Q, respectively. Triangles mean longitudinal polarization. Lines are a guide to the eye.

As exceptional details of the electronic spectra near the Fermi energy are reflected in anomalies in the phonon spectra, we have investigated the low frequency phonons via inelastic neutron scattering (INS) at $T = 50$ K close to the CDW transition, and also along off-symmetry directions close to the wavevector $Q = (a^*/3, 0, 0)$.

2. Experimental details

The inelastic neutron scattering experiment was carried out on the three-axis spectrometer IN8 at the Institut Laue-Langevin, Grenoble, France. The instrument was set up in a W configuration. We have used a Cu(200) monochromator and a PG(004) analyser. The data have been taken at $k_F = 4.1$ Å^{-1} and with a collimation of 40′–40′–40′–60′. The single crystal in the form of a platelet about $9\times5\times0.5$ mm^3 in size was mounted with the [ξ00]–[00ξ] directions in the scattering plane. We achieved an energy resolution of about 1 meV.

3. Results

3.1. Low frequency phonon dispersion at 50 K

We have investigated the longitudinal low frequency phonon branches with inelastic neutron scattering at some selected points at $T = 200$ K. More extensive measurements have been performed for the lower frequency modes at $T = 50$ K. We focused on their frequency, width and intensity distribution in proximity to the wavevector $Q = (a^*/3, 0, 0)$.

Figure 1 shows measured inelastic data at 200 K in comparison with room temperature data from Murphy *et al* [9] (left panel) and our data obtained with constant energy and constant Q scans for the low energy region at 50 K (right panel).

At 200 K we found agreement with existing room temperature data for bulk 2H-$NbSe_2$, e.g. [9], with only a slight deviation for the lower branch (see also the left panel of figure 1). At RT at $q = 0.33a^*$ a value of 6.8 meV for ω_1 is observed [9] (an even greater softening with a value of 4 meV is observed there for the ω_1 mode at the surface, pointing to a different electronic behaviour in comparison to that of the bulk).

At 50 K, close to the CDW transition at about 35 K, constant E and Q scans have been performed in the [ξ00] direction up to 12 meV in predominantly longitudinal geometry (right panel of figure 1).

At the zone centre a Raman active mode (E^2_{2g}) exists in the low frequency region (denoted with a circle in the left panel of figure 1) which seems to show barely a change with temperature. Measurements at RT [11] and at 80 K [13] report for this Raman mode a frequency of 3.7 meV.

We found a softening of the LA mode ω_1 attributed to Σ_1 symmetry with a broad minimum around $Q = (a^*/3\,0\,0)$ and a minimum energy of about 4 meV. The low lying LO mode (ω_2) of the same symmetry seems to experience a similar softening at the same Q value and an energy of about 5.5–6 meV in the minimum.

The value for the ω_1 mode is in agreement with the softening found by Ayache *et al* [10] at about 50 K. They obtained a value of about 2.3 meV at 35 K. Whether the ω_1 mode experiences a complete softening when approaching $T_{CDW} \approx 33$ K remained unclear within experimental accuracy. In comparison, 2H-$TaSe_2$, which has a transition temperature $T_{CDW} \approx 122$ K and a lock-in transition at about 90 K, shows a gap of about 4 meV [8] at the CDW transition temperature.

We found a broadening in the width of the constant energy scans especially around the minimum at about one third along the [ξ00] direction. From the constant Q scans the peaks close to the zone centre and zone boundary were especially visible. The other data were better resolved in the constant energy scans.

We could not find particular differences in the widths of the two modes ω_1 and ω_2 as was detected in [10] when following their temperature dependence from 100 K downwards.

3.2. Study of the phonon anomaly in the off-symmetry direction

To further study the phonon anomaly appearing, constant energy scans away from the [ξ00] direction for different q_z were taken along $Q = [2.5, 0, 0]$–$[3, 0, 0]$ at 3.5 and 4 meV (left and right panel of figure 2, respectively).

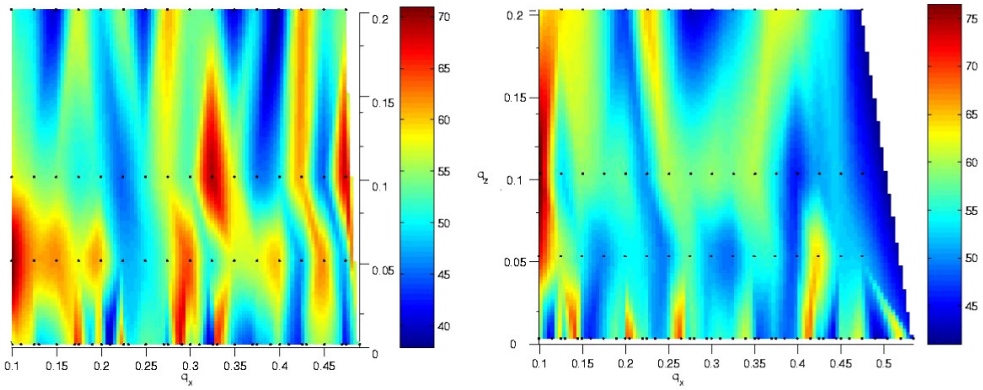

Figure 2. Constant energy scans in the $[\xi, 0, q_z]$ direction for $q_z = 0$, 0.05, 0.1 and 0.2 at 3.5 meV (left panel) and 4 meV (right panel) at 50 K.

At $q_z = 0$, along the main symmetry direction, the cuts with the intensities found for the dispersion at 3.5 and 4 meV, see figure 1, are visible. However at 3.5 meV mainly tails of the dispersion can be traced. The minimum of the anomaly appears there at $q_z = 0$ between $q = 0.29$ and 0.33, see the left panel of figure 2. For increasing q_z a slight tendency to smaller q_x emerges. But for further increasing q_z, i.e. $q_z = 0.1$, the minimum at $q = 0.33$ moves to lower energies.

At 4 meV for $q_z = 0$, again the cuts with the dispersion can be seen at about $q = 0.22$, 0.26, 0.34 and 0.42. For increasing q_z the minimum is clearly visible but weaker and slightly shifted to about $q = 0.3$. In addition, peaks arise near $q_x = 0.35$ and 0.25 (at $q_z = 0.1$) with their splitting becoming larger with increasing q_z.

4. Conclusions

The lattice dynamics of the quasi-two-dimensional layered transition metal dichalcogenides has been studied with INS at 50 K close to T_{CDW}. The dispersion has been followed along the whole Γ–M direction in mainly longitudinal geometry for the low frequency region.

We found a clear softening of the longitudinal acoustic and optic modes both attributed to Σ_1 symmetry with a minimum close to the incommensurate CDW wavevector $Q = (a^*/3, 0, 0)$. Investigations away from the main symmetry direction $[\xi 00]$ indicated that the anomalously low frequency at $Q = (a^*/3, 0, q_z)$ seems to further soften with increasing q_z, the real minimum not being along the main symmetry direction. The minimum appears weaker for 4 meV than for 3.5 meV. For increasing q_z a splitting becoming larger arises. Whether this function is really isotropic has still to be determined.

Further investigations are planned to pin down the precise position and function in q_x–q_z space and in energy. The behaviours for in-plane and perpendicular directions are expected to be quite different. The experimental determination of the temperature dependence and wavevector dependence of the anomalous frequency, width and intensity would supply an indirect determination of the electron–phonon coupling constants which are of central importance for this material. The measurement in off-symmetry directions will give information about its q-dependence.

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