



Title	Direct Electron-Diffraction Evidence of Charge-Density-Wave Formation in NbSe ₃
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Lett. **30**, 220 (1973).

²¹R. Chang and L. M. Falicov, *J. Phys. Chem. Solid* **32**, 465 (1971), showed that a pseudopotential procedure

which yields satisfactory lattice-vibrational spectra predicts negative (unphysical) values for the heat of formation of vacancies in metals such as Al.

Direct Electron-Diffraction Evidence of Charge-Density-Wave Formation in NbSe₃

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In NbSe₃ one-dimensional diffuse scattering was observed above 140 K and the satellite spots at a lower temperature. They correspond to the Kohn anomaly and the superlattice coupled with charge-density wave, respectively. The superlattice was found to be incommensurate, with the period $a' = a$, $b' \approx 4.1b$, and $c' = c$.

Recently, the transition-metal trichalcogenides MX_3 (M : Nb, Ta; X : S, Se) have been the subjects of several investigations.¹⁻⁶ These needle-shaped materials have the chain structure of the transition-metal atoms surrounded by the chalcogen atoms along the needle axis. The distance between metal atoms along the chain is much shorter than the interchain distances. Therefore the interactions between chains seem to be weak and one-dimensional behavior is expected in MX_3 .

One of the MX_3 family, NbSe₃, is characterized by two cusps in the temperature variation of the electrical resistivity along the b axis (needle axis) at 59 and 143 K. These anomalies have been explained by assuming the formation of a charge-density wave (CDW).¹⁻³ Especially the suppression of the two peaks in the resistivity by strong electrical fields is explained as Zener breakdown across the very small gaps at the Fermi surface induced by the formation of CDW.³ In this Letter we present the first direct evidence of CDW formation, by electron diffraction above 130 K.

NbSe₃ was synthesized by direct reaction of Nb and Se without carriers. The morphology and the resistivity anomalies of our crystals were the same as those reported by Haen *et al.*² The residual resistivity ratio was ~ 70 . It was found from x-ray diffraction studies with both the precession camera and the counter method, that the $(0k0)$ reflections were missing when $k = 2n + 1$. This extinction rule indicates that the space group of NbSe₃ is either $P2_1$ or $P2_1/m$, which have higher symmetry than Pm given by Meer-schaut and Rouxel.⁴ It seems that the presence

of the 2_1 screw axis along the needle axis is a common feature of MX_3 .⁷⁻⁹ The electron diffraction of NbSe₃ was performed with the acceleration voltage of 100 kV. The sample holder was kept at 130 K. But the temperature of the individual crystal may be slightly higher as a result of irradiation by the electron beam, though a heat link to the sample holder would release some of the heat.

Figure 1 shows the b^*-c^* plane of the reciprocal space above 140 K. The anomaly in diffuse scattering can be clearly seen to be one-dimensional. The position of this one-dimensional anomaly along the b^* axis is $(0.244 \pm 0.004)b^*$, which is a little smaller than the commensurate value of $0.25b^*$. This incommensurate streak

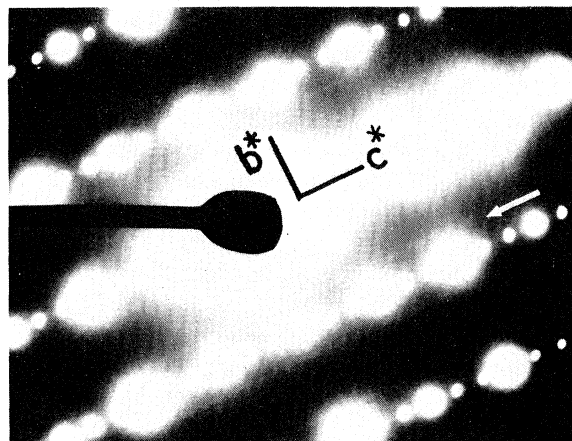


FIG. 1. Electron diffraction pattern of NbSe₃ above 140 K, showing one-dimensional anomaly in diffuse scattering (marked by arrows).

corresponds to the Kohn anomaly. In Fig. 2, which shows the a^*-b^* plane below 140K, the satellite spots are exactly at the position of the Kohn anomaly. From a similar observation on the b^*-c^* plane below 140 K, it was found that the satellite spots have no a^* and c^* components, at least at this temperature. These observations establish that an incommensurate superlattice with $a'=a$, $b'\approx 4.1b$, and $c'=c$ occurs in NbSe_3 . The incommensurability itself is a strong support of the CDW mechanism. Thus our electron diffraction experiments confirmed the existence of CDW in NbSe_3 .

We reported that TaS_3 undergoes the Peierls transition at 220 K.⁶ Comparing the two materials, the following points are worth noting:

(i) The low-temperature phase of TaS_3 has the commensurate superperiod of $c'=4c$ within the accuracy of 1%, while it is incommensurate in NbSe_3 . (Note that the chain axis is the b axis in NbSe_3 and the c axis in TaS_3 .)

(ii) From the nearly equal periods of the one-dimensional modulation, it is expected that the Fermi surfaces of these materials have common features in the normal state, e.g., nearly the same relative position in the Brillouin zone.

(iii) TaS_3 is semiconducting below the transition temperature, while NbSe_3 remains metallic. The Fermi surface of NbSe_3 must be nonplanar. From the resistivity change below 140 K, we estimate that half of the Fermi surface vanishes at the transition.

(iv) In TaS_3 the coexistence of the diffuse lines at $0.25c^*$ with satellites was observed, while in NbSe_3 the diffuse lines are absent below the transition as shown in Fig. 2. The diffuse streak connecting the parent spots perpendicular to the chain axis was often observed in both materials. It was not determined whether the diffuse streak is due to the soft phonon mode or the poor crystallization.

(v) In TaS_3 the satellite spots also have components perpendicular to the chain axis,¹⁰ while in NbSe_3 only the component along the chain axis was observed.

We could not extend the electron diffraction study below 130 K because of the limitation of our cooling apparatus. It must be very interesting to determine the nature of the 59-K anomaly.

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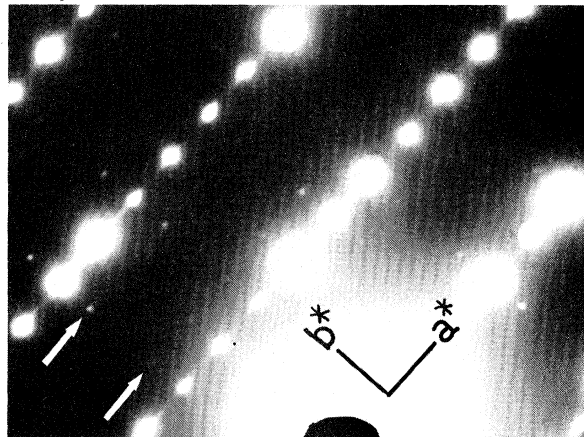


FIG. 2. Electron diffraction pattern of NbSe_3 below 140 K, showing the satellite spots (marked by arrows).

Laboratory for valuable discussions and Mr. H. Kuwahata of Department of Metallurgy for his skillful assistance in electron diffraction measurement.

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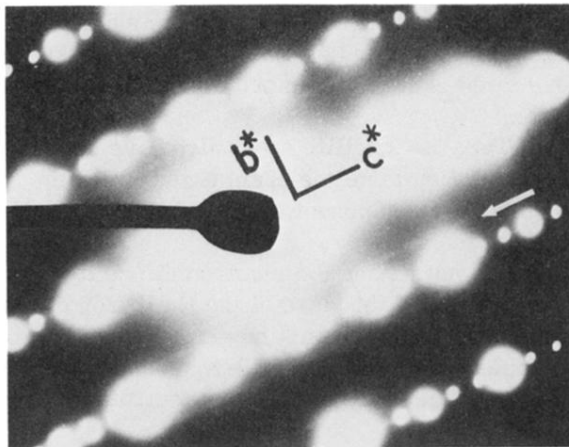


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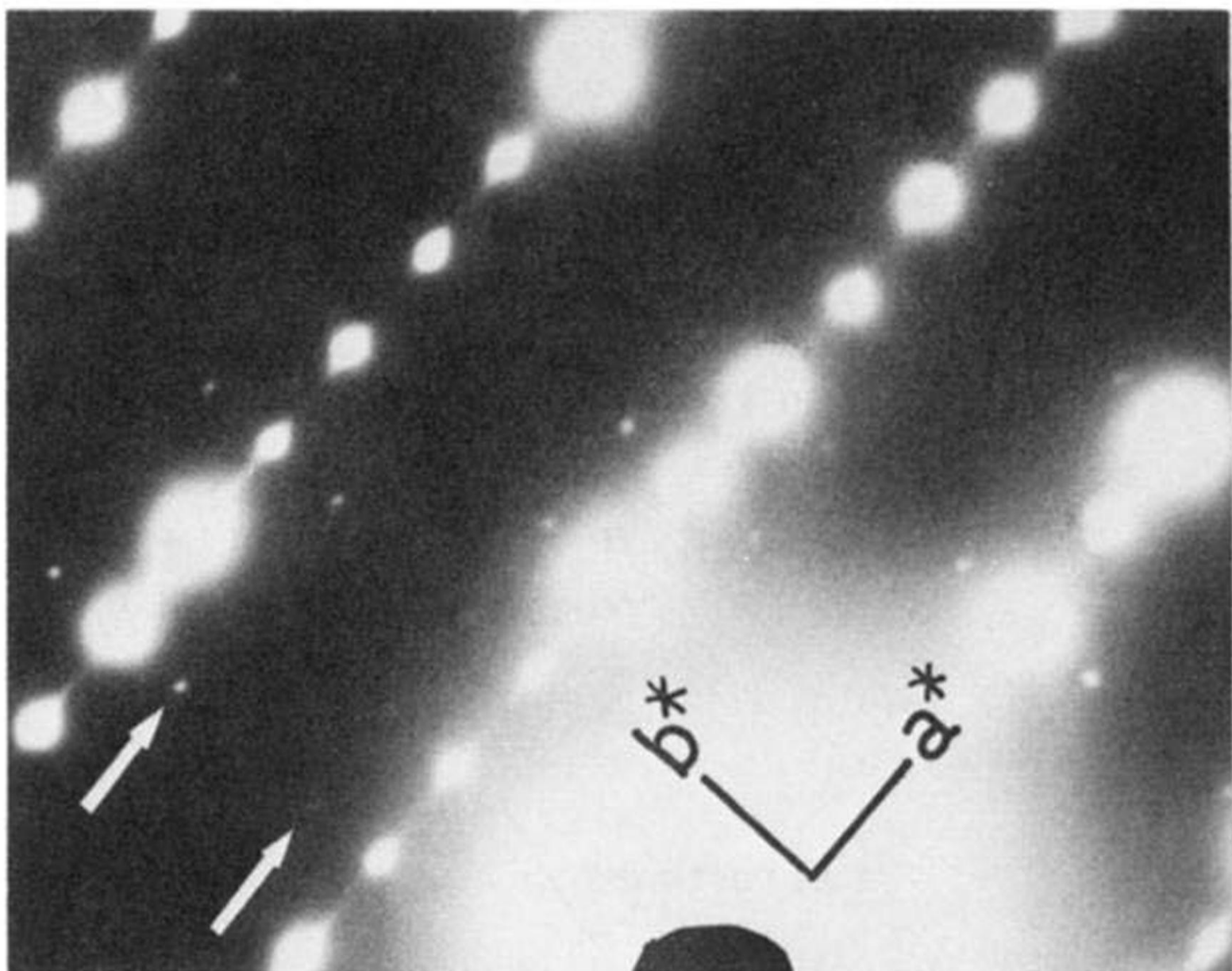


FIG. 2. Electron diffraction pattern of NbSe_3 below 140 K, showing the satellite spots (marked by arrows).