CORRESPONDENCE

Diffraction evidence for the Kohn anomaly in 1T TaS_2

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[Received 8 February 1974]

Abstract

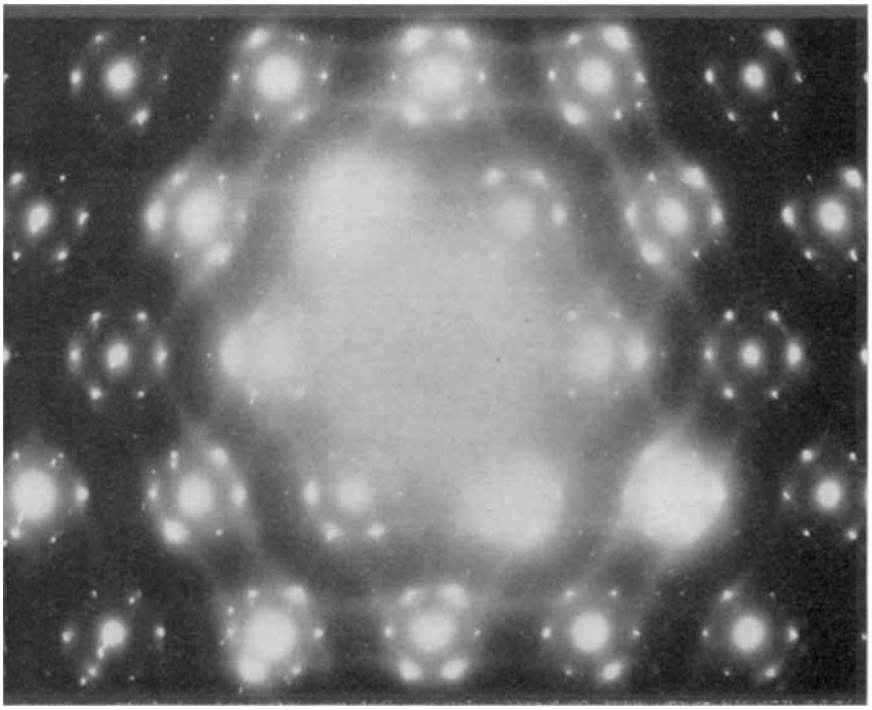
Diffraction studies have enabled the deformation structure of 1T TaS_2 to be interpreted in terms of charge density waves arising from a Kohn anomaly. There is good agreement between the observed periodicity of the lattice distortion and the value predicted from a Fermi surface based on recent band structure calculations.

Wilson and Yoffe (1969) reported that transmission electron diffraction studies of the metastable 1T phase of TaS_2 at room temperature gave a complex diffraction pattern, and suggested as possible explanations of this either a shear structure or an excitonic insulator phase. Our current diffraction studies reveal that the room-temperature phase ($1T_2$) undergoes a reversible transition to a second metastable phase $1T_1$ at about 350 K, which is the temperature of the semiconductor-metal transition reported by Thomson, Gamble and Revelli (1971). We also find a transition to a structure ($1T_3$) corresponding to that observed in resistivity data by these authors at 190 K.

The selected area diffraction pattern at 420 K (figure 1) shows not only the hexagonal matrix of reflections $\{\mathbf{M}\}$, corresponding to the ideal CdI_2 structure (space group $P\bar{3}m$ (D_{3d}^3)), but also the six extra reflections $\{\mathbf{S}_M\}$ which surround each matrix reflection; additional continuous scattering is also a prominent feature. Comprehensive electron and X-ray single crystal diffraction studies (to be published separately) reveal that $\{\mathbf{S}_M\}$ forms an octahedron about $\mathbf{M}$, two groups of three reflections in $\{\mathbf{S}_M\}$ making equilateral triangles, parallel to the $hk.0$ plane of $\{\mathbf{M}\}$, and at heights $(l \pm \frac{1}{3})c^*$ from the plane (l integral for $\{\mathbf{M}\}$). Thus the $\bar{3}$ axis in $\{\mathbf{S}_M\}$ is parallel to $\bar{3}$ in $\{\mathbf{M}\}$. Above 350 K there is complete coincidence between the $\bar{3}m$ symmetries for $\{\mathbf{M}\}$ and for $\{\mathbf{S}_M\}$, so that the reflections in $\{\mathbf{S}_M\}$ project on to the axes of $\{\mathbf{M}\}$. In the room-temperature phase this symmetry coincidence is lost, and there is an angle of 12° between the reflection planes in $\{\mathbf{M}\}$ and those in $\{\mathbf{S}_M\}$. Since the magnitude of the vectors joining $\{\mathbf{S}_M\}$ to the parent $\mathbf{M}$ is almost the same for the two phases, the transition is seen in diffraction as a re-orientation of the octahedron of extra reflections. Heating $1T_1$ TaS_2 to above 450 K changes it irreversibly to the stable 2H phase, when all the extra structure in the reciprocal lattice

disappears leaving a hexagonal matrix. The continuous scattering visible in fig. 1 is not observed at all in the room-temperature phase $1T_2$ and becomes strong as the temperature is raised close to the $1T_1$–2H transition temperature.

Fig. 1



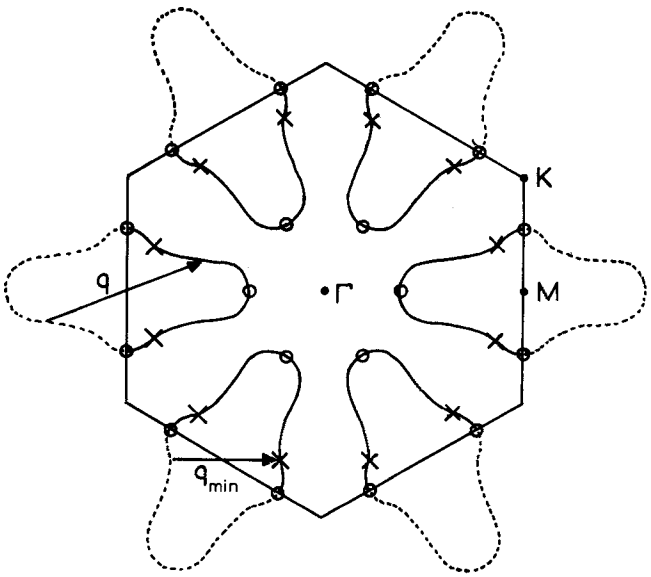
Selected area diffraction pattern of $1T_1$ TaS_2 at 420 K, showing *hk*.0 section of reciprocal lattice.

As far as can be determined, the periodicities in direct space which correspond to $\{\mathbf{S}_M\}$ are not commensurate with the crystal lattice defined by $\{\mathbf{M}\}$. Consequently the structure cannot be directly compared with those of the distorted tellurides, such as WTe_2 where the two-dimensional unit cell doubles in size (Brown 1966). The possibility of 1T TaS_2 having a shear structure must also be ruled out on the grounds that the matrix remains trigonal. The six extra reflections in $\{\mathbf{S}_M\}$ are most simply interpreted as resulting from three symmetry-related periodic lattice distortions of wavelength about 10·4 Å located in each TaS_2 layer. The Fourier transform of this in reciprocal space is a family of rods perpendicular to the TaS_2 layer. The relative phases of the distortion waves in adjacent layers produce a modulation along these rods: they reinforce at $(l+\frac{1}{3})c^*$ or $(l-\frac{1}{3})c^*$ and destructively interfere (making the structure factor zero) elsewhere. For the purposes of interpreting

Bragg scattering, a reduced cell scheme can be used whereby all the atom positions are translated to one unit cell of the distortion. For a non-commensurate periodic distortion in an infinite lattice, no atom positions exactly superimpose, and the situation is equivalent to forming a distortion wave in a continuous medium. The diffraction evidence in $\{\mathbf{S}_M\}$ implies that such distortions can be regarded as stacking rhombohedrally in adjacent layers without reference to the matrix structure.

The continuous streaks in the diffraction pattern of fig. 1 are indicative of phonon scattering, suggesting an interpretation of the periodic lattice distortions as a consequence of a Kohn (1959) screening anomaly. The latter occurs when there is a singularity in the static dielectric constant $\epsilon(\mathbf{q},0)$, resulting in an anomalously high polarizability of the lattice for a perturbation of wave vector $\mathbf{q}$ when $\mathbf{q} \simeq 2\mathbf{k}_F$. In terms of the Fermi surface, the anomaly can therefore be envisaged as resulting from the scattering of electrons across electron surfaces by phonons of wave vector $\mathbf{q}$. Having interpreted the reflections $\{\mathbf{S}_M\}$ as arising from a distortion modulating the ideal CdI_2 structure, we further propose that the reciprocal vectors joining each matrix reflection to the reciprocal lattice rods on which the $\{\mathbf{S}_M\}$ lie, correspond to wave vectors $\mathbf{q}$ satisfying the Kohn condition. The intensities of the discrete reflections $\{\mathbf{S}_M\}$ suggest that the strength of the electron-phonon interaction may be

Fig. 2

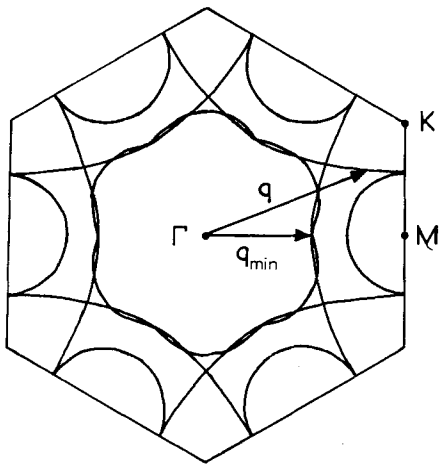


ΓKM (*hk*.0) section of the Brillouin zone showing the Fermi surface for 1T TaS_2, with two wave vectors $\mathbf{q}$ and $\mathbf{q}_{min}$ which satisfy $\mathbf{q} \simeq 2\mathbf{k}_F$, the condition for a Kohn anomaly. ○ data points from APW band structure calculations (Mattheiss 1973). × values of k_F determined from diffraction data.

sufficient to soften this mode completely, producing a charge density wave (Halperin and Rice 1968). From purely geometrical considerations, we also expect the measured $\mathbf{q}$ to correspond to the minimum wave vector which can produce Kohn scattering, i.e. $\mathbf{q}_{\min}$. The increase in intensity of the reflections $\{\mathbf{S}_M\}$ with h, k and with l indices in X-ray diffraction measurements, does in fact imply that there is strong coupling with LA phonons, and also some coupling with $TA_\perp$ modes. The phonon dispersion relationship measured by neutron scattering for MoS_2 (Wakabayashi, Nicklow and Smith 1972), which should be similar to that for TaS_2, indicates that the LA and $TA_\perp$ modes are sufficiently close in energy near the measured $\mathbf{q}$ value for there to be coupling with both, and that an unsoftened mode with this wave vector has an energy of ~ 20 meV and so is comparable with k_BT at the temperature in question.

Figure 2 shows a ΓKM ($hk.0$) section of the Fermi surface for 1T TaS_2 on which have been plotted points taken from the APW band structure calculations of Mattheiss (1973) for this material. Although these points themselves are interpolated between data calculations for high-symmetry points in the Brillouin zone, there is clearly a closed electron surface centred on M. The experimentally determined values of $\mathbf{q}_{\min}$ enable further points to be plotted on the Fermi surface for which $2(\mathbf{k}_F)_{\min} = \mathbf{q}_{\min}$. Having drawn closed electron surfaces to pass through these points, all values of $\mathbf{q}$ which satisfy the Kohn condition can be plotted out as in fig. 3. The result is in good agreement with the continuous scattering observed at higher temperature in the diffraction pattern, confirming that the Fermi surface of fig. 2 is of the correct form. The value of $\mathbf{q}$ in a direction parallel to ΓM and satisfying the Kohn condition for a given surface is most sensitive to the width of the surface along

Fig. 3



TKM section of the Brillouin zone showing all phonon wave vectors which satisfy $\mathbf{q} \simeq 2\mathbf{k}_F$ for the Fermi surface of fig. 2.

MK, and indeed a value predicted from the APW calculations for this dimension does give good quantitative agreement with $\mathbf{q}_{min}$ measured from diffraction. Again, the magnitude of $\mathbf{q}$ only increases very slightly from that of $\mathbf{q}_{min}$ in a direction of 12° to ΓM, as expected if the room-temperature phase $1T_2$ is to have a lattice distortion of very nearly the same periodicity.

Tosatti and Anderson (1974) argue that in an essentially two-dimensional material like 1T TaS_2, a complete softening of the phonon mode by the joint effect of electron-phonon and electron-hole interactions could result in the formation of an excitonic insulator ground state. This would account for the fact that at room temperature the material is a narrow-gap semi-conductor rather than a metal. Finally, we note that

(i) the energy of an unsoftened mode of wave vector corresponding to $\mathbf{q}_{min}$ measured from diffraction, extrapolated from the dispersion relation referred to above (Wakabayashi *et al.* 1972),
(ii) the energy of a phonon compatible with the width of a Fermi surface inferred from the band structure calculations (Mattheiss 1973),

are in close numerical agreement.

ACKNOWLEDGMENTS

We thank Dr. F. Levy (École Polytechnique Fédérale de Lausanne) for the supply of single crystals, and Mrs. B. A. Robinson for assistance with the electron microscopy.

Note added in proof 25 *March* 1974.—Similar effects have been observed in 1T TaS_2 and 1T $TaSe_2$ by J. A. Wilson, S. J. Di Salvo and S. Mahajan, 1974, *Bull. Am. phys. Soc.*, **19**, 347–349

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