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¹J. P. McTague, M. Nielsen, and L. Passell, Crit. Rev. Solid State Sci. <u>8</u>, 125 (1979), and references therein.

²T. T. Chung, unpublished, as quoted in F. E. Hanson, M. J. Mandell, and J. P. McTague, J. Phys. (Paris) <u>38</u>, C-76 (1977). ³B. I. Halperin and D. R. Nelson, Phys. Rev. Lett. <u>41</u>, 121 (1978), D. R. Nelson and B. I. Halperin, Phys. Rev. B (to be published).

⁴Hanson, Mandell, and McTague, Ref. 2.

⁵M. J. Mandell, J. P. McTague, and A. Rahman, J. Chem. Phys. <u>64</u>, 3699 (1976), and 66, 3070 (1977).

⁶F. E. Hanson and J. P. McTague, to be published. ⁷N. D. Mermin, Phys. Rev. <u>176</u>, 250 (1968).

⁸R. M. Cotterill, E. J. Jensen, and W. D. Kristensen,

in Anharmonic Lattices, Structural Transitions and

Melting, edited by T. Riste (Noordhoff, Leiden, 1974).

⁹F. Tsien and J. P. Valleau, Mol. Phys. <u>27</u>, 177 (1974).

¹⁰S. Toxvaerd, to be published.

¹¹D. Henderson, Mol. Phys. <u>34</u>, 301 (1977).

Direct Observation of Charge-Density Waves by Molecular-Beam Diffraction

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Using molecular-beam diffraction we have observed surface corrugation effects due to charge-density waves in TaS_2 . Satellite peaks have about the same intensity as Bragg peaks, contrary to results obtained from electron, neutron, and x-ray diffraction.

The question this paper wants to address is the following: Do charge-density waves (CDW) propagate up to the topmost layer of a crystal? If so, will the set of satellite wave vectors be the same as those observed in the bulk? Low-energy electron diffraction (LEED) experiments¹ on 1T-TaS₂ suggest indeed that the surface structure of this layered compound is almost identical to that of the bulk. A LEED beam directed into a crystal penetrates a small but finite number of atomic layers so that we can say that a LEED diffraction pattern reflects the average structure over, say, the first four or five atomic layers.

If a beam of neutral atoms, instead of slow electrons, is used in a diffraction experiment, only the very first atomic layer is involved in the scattering process, and a diffraction pattern obtained in these conditions reflects the corrugation of the surface, on the atomic scale, resulting from the crystalline periodic potential.²

While x-ray, neutron, or electron diffraction patterns reflect oscillations of the potential in the bulk, even though in the case of LEED by "bulk" we mean a crystal slice four or five atomic layers thick, a molecular-beam diffraction pattern can be interpreted strictly in terms of scattering from a hard corrugated surface, whose shape z = f(x, y) can be obtained from the intensities of the diffraction peaks.³

We selected $1T-TaS_2$ as a crystal suitable for this experiment because the various superstructures at different temperatures are well known,⁴ and, given the good results obtained on graphite,⁵ it was expected that a layered compound would in general give good diffraction patterns with molecular beams after cleavage in air along the layer planes.

The experiment was done using a He beam with $K_0 = 2\pi/\lambda = 11.05 \text{ Å}^{-1}$. The experimental setup has been described in detail elsewhere.⁶ A 1T-TaS₂ crystal, previously checked with x rays to really be the 1T polytype, was fastened with Aquadag⁷ to a sample holder that could be heated up to high temperature in order to clean the surface in vacuum. The sample holder could be rotated around the normal to its surface by means of an external manipulator. Good vacuum was obtained by cryopumping with liquid helium in proximity of the crystal.

Care was taken to avoid heating the crystal above 450° K, at which temperature the 1*T* polytype transforms irreversibly to 2*H*, which does not exhibit any superstructure at 80° K.⁸ All experiments were done with the crystal at about 80° K. VOLUME 42, NUMBER 24

At this temperature the crystal is in the $1T_3$ form,⁴ with a set of commensurate distortions defining a reduced reciprocal cell $(a' = a_0\sqrt{13})$, rotated by $13^{\circ}54'$ with respect to the main lattice. Figure 1 shows the (hk) reciprocal plane, and the relationship between Bragg spots and satellite reflections. Figure 2 shows a profile taken along one of the principal directions of the hexagonal net defined by the satellite reflections, corresponding to the line (00)-*G* of Fig. 1. In this scan the crystal is kept stationary at fixed incidence (indicated herein), and the counter is rotated around the crystal on the equatorial plane. All the peaks shown in Fig. 2 correspond to superlattice reflections in accord with the $\sqrt{13} \times \sqrt{13}$ structure.

Figure 3, curve *a* shows a similar scan along the (10) direction. This scan was used to set the azimuthal orientation of the crystal. The azimuth was adjusted to correspond to maximum intensity for the plane at $\theta_f \simeq 42^\circ$, where the (10) was expected to be found. It was also checked that the two closest superlattice reflections to the line (00)–(10) (see Fig. 1) among the six nearest neighbors to (10), were found where expected.⁹ Figure 3, curve *a* shows unmistakably the presence of well-developed Bragg peaks up to the second order, which indicates an appreciable degree of surface corrugation.



FIG. 2. The scan proceeds along the dotted line (00)-G in Fig. 1. All the peaks observed in this profile, except for peak I (unidentified), correspond to chargedensity waves. The angle of incidence is fixed at θ_i = 60°. Helium atoms are impinging on the crystal, with $K_0 = 2\pi/\lambda = 11.05 \text{ Å}^{-1}$. The angle on abscissa, θ_f , is the angle at which the counter aperture is located on the equatorial plane. Both angles θ_i and θ_f are evaluated with respect to the surface normal. (00) is the specular beam. The numbers indicated along the vertical axis correspond to absolute reflectivity values.

It is also clear from Fig. 3 that extra peaks show up in the diffraction pattern. Peaks P and K, for example, correspond to the positions



FIG. 1. (hk0) plane of $1T_3$ -TaS₂. One set of superlattice reflections is present, defining a $\sqrt{13} \times \sqrt{13}$ commensurate superstructure. The set is tilted by $13^{\circ}54'$ counterclockwise with respect to a (10) direction. Circled points and squares indicate observed peaks in Figs. 2 and 3.



FIG. 2. Solid curve a: Scan along the (0h) direction. Dotted curve b: The crystal has been rotated by 6° counterclockwise. The scan proceeds along the line (00)-T' of Fig. 1. Bragg peaks up to the second order are clearly visible. Other peaks labeled by primed and umprimed capital letters are due to charge-density waves. Along the vertical axis, left numbers are referred to profile a, right numbers to profile b.

marked as *P* and *K* in Fig. 1. Since the detector slit defines a vertical divergence (normal to the diffraction plane) of about 2° , it is not surprising that peaks located at azimuths $4^{\circ}-5^{\circ}$ off the diffraction plane can still contribute an appreciable signal into the detector. All the extra peaks present in Fig. 3, curve *a* can be correlated with superstructure reflections.

When the crystal is rotated by 6° around the normal to the basal planes, the dotted line is obtained. The value and the direction of the azimuthal rotation (6° counterclockwise, looking at the crystal surface) were chosen in such a way as to maximize the intensity of peak K, called K' in profile b. The (10) peak (now called M') becomes weaker, as expected, and the (20) disappears, but the superstructure peaks K' and T' are stronger, which is related to the fact that now the scanning proceeds along the (00)-T' line in Fig. 1.

The locations of the peaks observed in Figs. 2 and 3 are indicated in Fig. 1. It is clear that every observed peak can be attributed to a Bragg spot or to a superstructure reflection, with a couple of possible exceptions, such as the small peaks P' and I, in Figs. 3 and 2, respectively, for which we have no explanation. It is not clear, either, why peak Z' in Fig. 1 does not show up in Fig. 3.

What is surprising, however, is that superstructure reflections have about the same intensity as Bragg peaks in a molecular-beam diffraction pattern, as opposed to x-ray, neutron, or electron diffraction, in which case they are about 20-50 times weaker.

Note how well developed are certain superstructure peaks such as K' in Fig. 3, curve b and peak A in Fig. 2, which are comparable to the strongest Bragg peaks such as the (00) and the (10) in Fig. 3, curve a.

The reason for this difference must be searched in the intrinsic mechanism of scattering of neutral atoms from surfaces. In this case it is the corrugation of the electron sea at the surface that determines the features of a diffraction pattern.

It is conceivable that what is observed here is the *real* effect of scattering from a CDW corrugated electron sea, as opposed to an x-ray, neutron, or electron scattering experiment, in which what is observed is the *reaction* of the positiveion lattice to the charge modulation. The latter effect is much smaller than the primitive phenomenon, which generates a periodic lattice distortion. A rough estimate for potassium¹⁰ predicts a value for the fractional charge modulation of the electrons $p \simeq 0.17$, corresponding to a ratio $I(2\pi \vec{G} \pm \vec{Q})/I_0$ of superstructure reflections to Bragg reflection intensities of the unmodulated lattice of the order of 7×10^{-3} . It may not be surprising, therefore, that in molecular-beam diffraction patterns CDW superstructure reflections and Bragg peaks have comparable intensities.

We believe that molecular-beam diffraction has a great potential as a direct probe of instabilities displayed by systems of conduction electrons with respect to periodic perturbations.

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¹B. J. Mrstik, R. Kaplan, T. L. Reinecke, M. Van Hove, and S. Y. Tong, Nuovo Cimento <u>38B</u>, 387 (1977).

²See, for example, review article by G. Boato and

P. Cantini, in Dynamic Aspects of Surface Physics, Proceedings of the International School of Physics

"Enrico Fermi," Course LVIII, edited by F. O. Goodman (Editrice Compositori, Bologna, Italy, 1975).

³U. Garibaldi, A. C. Levi, R. Spadacini, and G. E.

Tommei, Surf. Sci. <u>48</u>, 649 (1975).

⁴C. B. Scruby, P. M. Williams, and G. S. Parry, Philos. Mag. <u>31</u>, 255 (1975).

⁵G. Boato, \overline{P} . Cantini, and R. Tatarek, Phys. Rev. Lett. <u>40</u>, 887 (1978).

⁶G. Boato, P. Cantini, and L. Mattera, Surf. Sci. <u>55</u>, 141 (1976).

⁷Manufactured by "Acheson Italiana S.r.l."

⁸J. P. Tidman, O. Singh, A. E. Curzon, and R. F. Frindt, Philos. Mag. <u>30</u>, 1191 (1974).

⁹After this experiment was completed, it was found that the procedure we followed for identifying the peak (10) could have led to a superlattice peak, instead of (10), if the system of superlattice reflections had been obtained by a $13^{\circ}54'$ rotation in a direction opposed to that postulated in Fig. 3. The main conclusions of this paper remain unaltered.

¹⁰A. W. Overhauser, Phys. Rev. <u>167</u>, 691 (1968).

Corrections to Dynamic Scaling for the Lambda Transition in Liquid Helium

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The noncritical background thermal diffusion is extracted from experimental data and found to be relatively strong. This produces large transient corrections in the critical relaxation rates. The *negative amplitude of the slow transient* strongly perturbs the entropy relaxation rate. Inclusion of *both slow and fast* transient yields an excellent fit with Ahlers's thermal conductivity data. Light scattering data are also well accounted for.

Because of the absence of inhomogeneities and elastic strains, fluids generally have sharper phase transitions than solids. Of all the fluid transitions, the λ transition in liquid ⁴He has been investigated with perhaps the greatest precision, with an accuracy for the reduced relative temperature, $t = (T - T_{\lambda})/T_{\lambda}$, of the order of 10^{-6} . It has been, therefore, a severe disappointment to theorists and experimentalists alike that in this "most favored" of phase transitions the agreement between theory and experiment appears to be not at all good. This situation has been reviewed by Hohenberg and Halperin.¹ Specifically, Ahlers² finds that the temperature dependence of the thermal conductivity above the λ point is significantly stronger than predicted by dynamic scaling theory. The purpose of this note

is to demonstrate that this discrepancy is only apparent. When certain natural and necessary corrections are included in the theory, remarkably good agreement is obtained with both the thermal conductivity measurements of Ahlers² and the light scattering measurements of Tarvin, Vidal, and Greytak.³ (We remain, however, unable to account for the surprisingly large secondsound damping observed by Tyson.⁴)

The correction that we treat here is associated with the noncritical background contributions to $\gamma_{S,\psi}$, the entropy and order-parameter relaxation rates. The importance of background thermal conductivity has been established by Keyes and Sengers⁵ for the normal fluids. Our goal here is to exhibit in full quantitative detail how background enters in the critical dynamics of the λ