X Ray Observation of $2k_F$ and $4k_F$ Scatterings in Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ)

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X-ray-scattering measurements on TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane) above 54 K clearly reveal a new one-dimensional scattering at the wave vector $(0.59 \pm 0.02)b^*$ interpreted as $4k_F$ scattering and attributed to an additional phonon anomaly which also condenses at low temperature. This $4k_F$ scattering is still clearly visible at 220 K in contrast to the earlier reported $2k_F$ scattering which is found to disappear at 150 K in agreement with the neutron scattering results of Shirane *et al.*

Since the initial reports of the existence of a low-temperature superlattice and Peierls transition in TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane)[1,2] considerable structural data have been accumulated on this compound.[3-7] The existence of three low-temperature phases due to condensed charge-density waves, with transition temperatures of 38, 49, and 54 K, is now established, and is relatively well understood in terms of two-chain descriptions.[8-13]

Above 54 K, one-dimensional (1D) precursor effects, attributed to the giant Kohn anomaly, were barely visible, and only briefly described in earlier x-ray studies. Two independent inelastic neutron-scattering investigations[5,6] have since reported observation of such a phonon anomaly at twice the Fermi wave vector, $2k_F = \pm 0.295b^*$, where b^* is the reciprocal lattice constant in the chain direction. Mook and Watson[5] have described a phonon anomaly visible and sharp up to room temperature while Shirane *et al.*[6] have reported an anomaly which develops only below 150 K.

The motivation of the present x-ray studies was twofold: firstly, to characterize more precisely the 1D features of the precursor effects above 54 K; secondly, to investigate their temperature dependence. We find that in addition to the scattering at $0.295b^*$ corresponding to $2k_F$ reported previously[1-7] a new scattering is observed [Fig. 1(a)] at $0.59b^*$ which is equivalent to $4k_F$. Moreover, the temperature dependence of the $2k_F$ scattering is in complete agreement with the inelastic neutron-scattering results of Shirane *et al.*[6] The newly observed $4k_F$ scattering displays a different temperature dependence, and is the only scattering visible above 150 K [Fig. 1(b)].

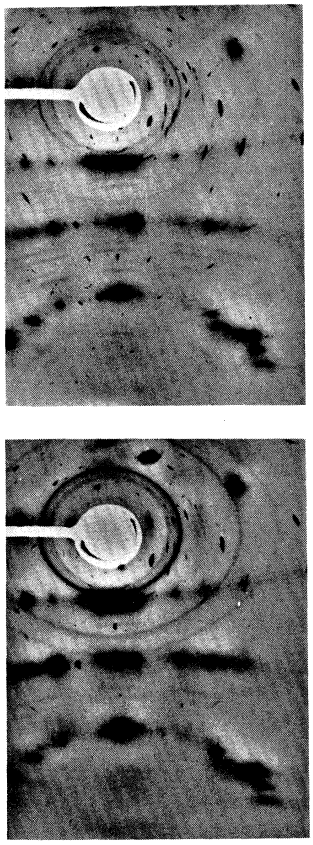

FIG. 1. Diffuse x-ray patterns of TTF-TCNQ ($\lambda = 1.54$ Å). Orientation of the sample: b^*, c^* horizontal; angle between x-ray beam and b^*, 124°. (a) At 60 K; $2k_F$ and $4k_F$ scatterings are clearly visible. (b) At 150 K; only $4k_F$ scattering can be observed. (The rings around the incident beam are powder parasites. Bragg spots with a $0.5b^*$ component are due to $\lambda/2$ contamination from the continuous spectrum of the x-ray source.)

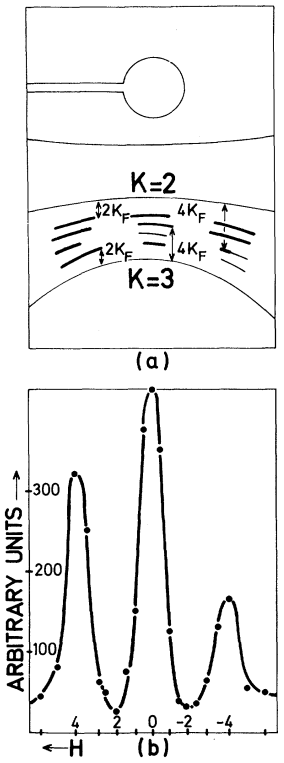

FIG. 2. (a) Schematic representation of the $2k_F$ and $4k_F$ diffuse scattering between $K=2$ and $K=3$. (b) Calculated form factors along the $k=2.295$ diffuse sheet from the pattern in Fig. 1(a). The calculation is made with equal amplitudes on both types of stacks. The points correspond to calculated values and the solid line is just a guide for the eye.

The intensity distribution of the diffuse scattering further agrees with the calculated scattering from *uncorrelated* waves on the molecular stacks (Fig. 2).

Since the earlier x-ray study,[1] the experimental conditions of our fixed-crystal, fixed-film technique[14] have been substantially improved. Large-size beryllium windows allowed the use of the more intense Cu $K\alpha$ radiation ($\lambda = 1.54$ Å) which is more suitable for the investigation of light material such as TTF-TCNQ. A double bent pyrolithic graphite monochromator of higher reflectivity (002 reflection) replaced the lithium fluoride monochromator. The cryocooled low-temperature camera, initially built for planar films, was transformed into a cylindrical one which allows higher scattering angles. These modifications altogether resulted in an effective intensity gain by a factor of the order of 25 (estimated from the exposure times).

High quality, untwinned crystals, identical to those of previous x-ray and neutron studies were used.

The unanticipated result of this investigation, as can be seen in the pattern taken at 60 K [Fig. 1(a)], is not only a clear observation of the 1D scattering at the wave vector $2k_F$ ($0.295b^*$) due to the expected Kohn anomaly, but also a second, previously unobserved 1D scattering. Within present experimental error of $\pm 0.02b^*$, this new scattering occurs at twice the former value, $0.59b^* \pm 0.02b^*$. On the basis of the previous assignment of $0.295b^*$ to $2k_F$, it would correspond to $4k_F$.

At first sight the $4k_F$ scattering might be thought of as arising from second-order diffraction from the $2k_F$ anomaly. This, however, is ruled out by the very different temperature dependence of the two types of scattering. At 60 K both scatterings exhibit comparable intensities [Fig. 1(a)]. When the temperature is increased the intensity of the $2k_F$ scattering decreases rapidly. At 130 K the $2k_F$ diffuse scattering is already broadened in the chain direction and is hardly observable; by 150 K it is no longer detectable [Fig. 1(b)]. This is in complete agreement with the temperature dependence of the $2k_F$ Kohn anomaly reported by Shirane *et al.*[6] and rules out the possibility of a sharp *phonon* anomaly at room temperature as reported by Mook and Watson,[5] which requires enhanced amplitude phonons at the wave vector $0.295b^*$. On the other hand, the temperature dependence of the $4k_F$ scattering is completely different; it remains sharp at 150 K [Fig. 1(b)], is clearly visible at 220 K, and becomes weaker but is still observable at room temperature.

The absolute intensity of the diffuse scattering compared to Bragg reflections is difficult to extract from such photographic measurements because of the considerable difference between them. It is also not very meaningful since densitometer readings from diffuse lines due to phonon anomalies will only provide the intensity enhancement at the wave vectors $2k_F$ and $4k_F$ compared to that of the regular phonons which produce the background. Compared to the intensity of the low-temperature $2k_F$ satellites, the 1D scattering is about 10^{-2} at 65 K. As the intensity of the satellites relative to the main Bragg peaks is known from previous measurements to be of the order of 10^{-4},[3] this yields a ratio of the diffuse scattering intensity compared to the main Bragg peaks of about 10^{-6} at 60 K (temperature at which the $2k_F$ and $4k_F$ scattering have comparable intensities), and of about 10^{-7} at 130 K

for the $2k_F$ scattering.

From microdensitometer readings, the correlation length in the chain direction (defined as the inverse half-width at half maximum expressed in inverse angstroms) can be estimated to be 100 Å at 60 K for both types of scatterings.

The satellite diffuse planes of TTF-TCNQ appear as interrupted diffuse lines, in contrast to the x-ray patterns from KCP $\{K_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O\}$[14] where continuous diffuse lines are observed. X-ray scattering from displacive phenomena, such as phonons, is proportional to the mean-square amplitude of the atomic displacements, weighted by the square of the atomic scattering factor. X-ray scattering reflects the larger-amplitude $2k_F$ wave-vector phonons, mainly for the platinum chains in KCP, giving rise to continuous diffuse satellite sheets. In the case of TTF-TCNQ, since most atoms have comparable scattering factors, the intensity variation along the diffuse lines reflects the phase differences between the x rays scattered from the different atoms of the displaced TTF and TCNQ molecular units (i.e., the eigenvectors of the $2k_F$ and $4k_F$ modes). A similar type of scattering was observed in TSeF-TCNQ (tetraselenafulvalene-TCNQ).[15]

A simple preliminary calculation was performed along the $2k_F$ sheet observed at $k=2.295b^*$ using the inelastic structure factor $F=\sum f_i(\vec{Q}\cdot\vec{u}_i)\exp(i\vec{Q}\cdot\vec{r}_i)$, where $Q=ha^*+kb^*+lc^*$ is the scattering vector; a^*, b^*, and c^* are the reciprocal lattice constants; f_i, u_i, and r_i are the scattering factor, the phonon amplitude, and the position of atom i, respectively. If we assume only translations of rigid molecules ($u_i=u$), no component of u in the a direction ($u_a=0$), and the main component of u in the b direction ($u_b>u_c$) as suggested in earlier work,[1,4] the inelastic structure factor reduces to a form factor $\sum_i f_i\exp(i\vec{Q}\cdot\vec{r}_i)$ ($k=$ const, l and u_c small yield $\vec{Q}\cdot\vec{u}\simeq k\vec{b}\cdot\vec{u}_b=$ const) for each molecule of the unit cell. As illustrated in Fig. 2, a good agreement with the general features of the intensity distribution is obtained if the four different molecular stacks of TTF-TCNQ are modulated independently from each other yielding intensity $I=F_1^2+F_2^2+F_3^2+F_4^2$. A similar result is obtained along the $4k_F$ sheet at $2.41b^*$ ($3b^*-0.59b^*$). This gives a clear confirmation of the truly 1D character of the two anomalies.

How much the newly observed $4k_F$ scattering will modify the present picture of the low-temperature modulated lattices is not yet known. Only a few temperatures have been investigated below 54 K. Additional weak superlattice reflections with a $4k_F$ wave-vector component have been clearly observed at 25 K, but their wave-vector components in the a^* and c^* directions are not precisely characterized (tentative values are $0.5a^*$ and $0c^*$). These superlattice reflections were not observable in a pattern taken at 45 K where only 1D $4k_F$ scattering was visible, confirming the different temperature dependence of the $2k_F$ and $4k_F$ anomalies.

By analogy with the successful description of the low-temperature modulated lattices in terms of two-chain models,[8-10] an attractive explanation of the occurrence of two anomalies is to assign the $2k_F$ scattering to one molecular species and the $4k_F$ scattering to the other. This approach provides a very simple physical picture, if one type of stack behaves as a normal 1D metal and gives rise to the expected $2k_F$ Kohn anomaly at the wave vector $0.295b^*$, and the other type of stack, because of particular electron interactions, gives rise to the second anomaly. Repulsive interactions between electrons in the strong-coupling limit[16] or the analog which could eventually arise from strong electron-optical phonon (or exciton) coupling[17] on one molecular species would require twice as many momentum states for the conduction electrons and double the Fermi wave vector, and give rise to a second anomaly at $4k_F$. Such an oversimplified description needs a detailed structural analysis of both types of scattering. Using a different model of strong Coulomb correlations, on both chains, Torrance[18] argued for the existence of two anomalies in TTF-TCNQ: The anomaly at $0.59b^*$ is associated with charge-density waves, while that at $0.295b^*$ is driven by spin waves. Another explanation using weaker coupling has been worked out by Emery.[19] The condensation of the $2k_F$ anomaly arises because the cost in elastic energy is more than balanced by the gain in electron energy from umklapp scattering of a *single* electron from one point on the Fermi surface to the opposite one. This opens a gap in the one-electron spectrum. By a similar process, the $4k_F$ anomaly can arise from the gain in energy from umklapp scattering of *two* electrons across the Fermi surface, causing a gap in the charge-density spectrum.

In this paper, we assigned the anomaly at 0.295^* to the $2k_F$ wave vector, as was done in the earlier reports[1-7] and the additional anomaly at $0.59b^*$ to the $4k_F$ wave vector. An alternative possibility is to assign the first anomaly to the wave vector k_F and the second to $2k_F$.

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Study of Surface Polaritons in GaP by Optical Four-Wave Mixing

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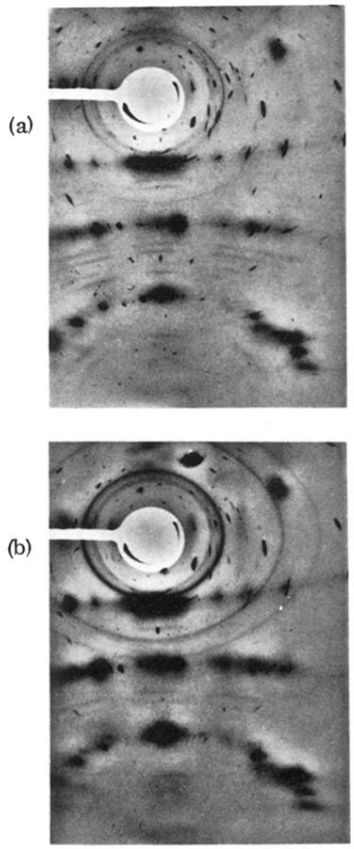
We demonstrate experimentally that optical four-wave mixing can be used to study surface polaritons in solids. The dispersion characteristics of surface polaritons in GaP are measured and compared with theoretical calculations.

Stimulated by the recent development in surface physics, there has been rapidly growing activity in the field of surface polaritons and plasmons. A large number of reports on the subject exist in the literature dealing with experimental investigation using various methods: inelastic electron diffraction,[1] attenuated total reflection,[2] grating coupling,[3] spontaneous Raman scattering,[4,5] etc. Studies of surface polaritons and plasmas can lead to information about oxide or molecular overlayers on semiconductor and metal surfaces.[5] Recently, two of us have proposed that the method of nonlinear excitation by optical mixing of laser beams can also be used to study surface polaritons and plasmons.[6] We have now succeeded in demonstrating experimentally the feasibility of the method in our laboratory. We used the four-wave mixing scheme[7,8] to excite coherently and to detect the surface polaritons in GaP and to measure their dispersion characteristics. In this Letter, we report the preliminary results of our experiment.

Before we venture into the experimental details, let us first briefly review the theory. We shall fol-



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