Experimental Evidence from X-Ray Diffraction for Phase Excitations in Solids

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The existence of phase excitations (phasons) in a solid with charge-density waves is clearly demonstrated in a diffraction experiment. It is found that a phason temperature factor, analogous to the usual Debye-Waller factor for phonons, must be introduced in interpreting diffraction data. At 90 °C, this factor attenuates all first-order satellites by a factor of 4.

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A number of years ago it was postulated by Overhauser that charge-density waves (CDW's) might exist in a solid as a result of exchange and correlation interactions among electrons.[1] The conditions under which CDW's can be observed in a diffraction experiment were investigated in a subsequent paper,[2] in which a new kind of excitation was postulated to exist in a crystal with CDW's: phase-modulation phonons, called "phasons." It is assumed that the phase φ of a CDW is time dependent, and that, similar to lattice displacements, it can be expanded into normal modes: $\varphi(\vec{L},t)=\sum_{\vec{q}}\varphi_{\vec{q}}\sin(\vec{q}\cdot\vec{L}-\omega t)$, where $\vec{L}$ is a lattice translation, $\vec{q}$ is the phason wave vector, and $\omega(\vec{q})$ is its frequency. Phasons are for CDW's the analog of phonons for atomic positions. They represent vibrations of the crests and troughs of CDW's. So far the existence of phasons has been inferred from anomalies in low-temperature specific-heat data of some metals and alloys,[3-5] and in point-contact spectroscopy experiments.[6]

In this paper we present unambiguous and convincing evidence, based on x-ray diffraction data, of the existence of phasons in a solid with CDW's: $1T$-TaS_2.

It has been shown in Ref. 2 that phasons give rise to a temperature factor, similar to a Debye-Waller factor, affecting CDW satellites. By taking the Fourier transform of a lattice with a phase-modulated CDW, it can be easily shown, using the same procedure that leads to the Debye-Waller factor, that a similar factor is obtained for phasons, *in which, however, the K^2 dependence is absent* ($K=2\pi\sin\theta/\lambda$). This factor, of the form e^{-CT}, is called phason temperature factor (PTF) and plays the same role for CDW satellites as the Debye-Waller factor for Bragg reflections. The absence of a K^2 dependence in the temperature dependence of CDW satellites is the typical signature of a PTF.

In this work we have measured with great accuracy, *on an absolute basis*, a number of first- and higher-order CDW satellites in $1T$-TaS_2 in the temperature range 25–150 °C. In this temperature range the crystal undergoes a polymorphic transition[7,8] at 80 °C between a quasicommensurate phase T_2 ($T<80$ °C) and an incommensurate phase T_1 ($T>80$ °C). Since, however, the data taken for the T_2 phase are difficult to understand, we will confine our attention in this paper to data taken in the *incommensurate phase* T_1 ($T>80$°C), for which a clear physical picture emerges. The CDW spots were located in reciprocal lattice using data given in the literature,[7] and confirmed by our own precession photographs (Fig. 1 is an example), which provide an undistorted view of reciprocal space. The same crystal was then transferred to a computer-controlled

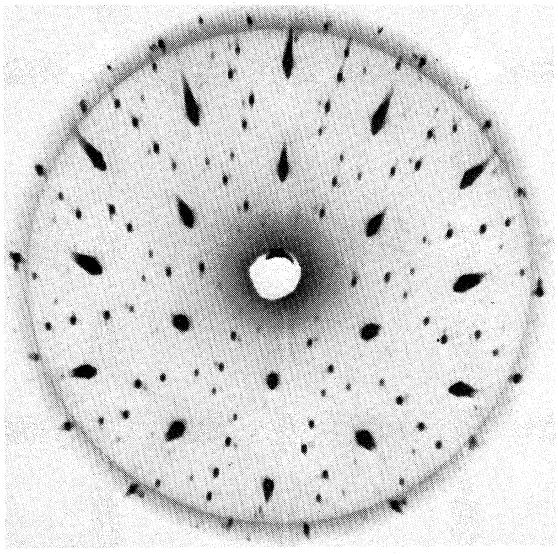

FIG. 1. Precession photograph of $1T$-TaS_2 at 25 °C. $(hk0)$ planes. The heavy spots are the Bragg reflections; all other spots are second- and higher-order CDW satellites. Mo $K\alpha$ radiation ($\lambda=0.71$ Å). Monochromator: flat graphite; 30 kV, 250 mA, 14.4 h. The streaks are due to incomplete monochromaticity.

diffractometer, and the integrated intensities of several spots were measured. A 12-kW rotating-anode x-ray generator was used for the precession photographs, whereas a conventional 1.8-kW generator was used for the data taken with the diffractometer. Mo $K\alpha$ radiation ($\lambda = 0.71$ Å) was used in this experiment, monochromatized by means of an asymmetric curved quartz crystal plate (Johansson type). The TaS_2 crystal, in the form of a thin plate[9] ($\simeq 5\times5\times0.04$ mm^3), was intercepting the whole beam (cross section: $\simeq 1 \times 0.2$ mm^2), whose intensity was measured using calibrated absorbers, so that each integrated intensity could be placed on an absolute basis. In Fig. 2 we show a semilogarithmic plot of six CDW-satellite intensities versus temperature, along with one Bragg reflection, the (030). It is apparent from Fig. 2 that all CDW satellites exhibit a more pronounced temperature dependence than the (030) Bragg refection. *More importantly, it is clear in Fig. 2 that all CDW satellites have essentially the same slope, within experimental error, even though the K^2 values associated with each plot vary from 2.5 to 46.* The slopes would be expected to vary proportionately to these extreme values for ordinary phononlike thermal factors. *We interpret the absence of a K^2 dependence in the slopes of Fig. 2 as the signature of a "phason temperature factor,"* which is responsible for the most part of the temperature dependence of the CDW satellites. The standard Debye-Waller factor is also operating on the slopes of Fig. 2. However, judged from the (030) Bragg reflection, also shown in Fig. 2, its effect must be much smaller, and, being unknown, can be neglected in our analysis.

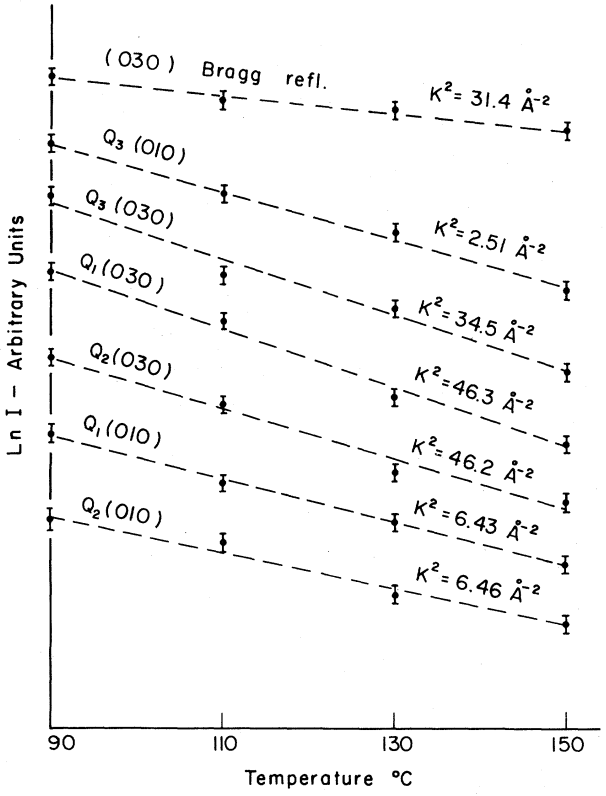

FIG. 2. Logarithm of integrated intensities of CDW satellites, and of the (030) Bragg reflections, vs temperature. Note the different K values for the satellite intensities. The (hkl) indices in parentheses are the Bragg reflections associated with each first-order satellite. The profiles have been arbitrarily shifted vertically for the sake of clarity.

As a final test of our assertion, namely, that the observed temperature dependence of Fig. 2 is governed by phasons, we have calculated the displacements of Ta and S atoms needed to produce the observed intensities for the six first-order satellites taken into consideration. An orthogonal set of unit displacement vectors has been introduced for each CDW: $\vec{U}_L{}^i$, $\vec{U}_T{}^i$, $\vec{U}_C{}^i$, ($i = 1,2,3$). They are, respectively, parallel to the basal projection of the CDW wave vector, perpendicular to the same projection, and parallel to the c axis. The following model has been used. All our precession photographs show, in agreement with the findings of Ref. 7, that all CDW satellites form a rhombohedral sublattice. We also found in our photographs that, in the incommensurate phase only, one of the three first-order spots, projected on a basal plane, is always located on the scattering vactor $\vec{G}$ of the Bragg reflection associated with the particular triplet of first-order satellites under consideration. This feature is not visible in Fig. 1 because in the ($hk0$) plane no first-order satellites are present, but it can be seen in photographs of the ($hk\frac{1}{3}$) plane, for example. This consideration allows us to assume, using symmetry arguments, that no transverse displacements are present. Each layer of Ta atoms is sandwiched between two sulfur layers, with strong binding forces between these three atomic planes. We assume that Ta atoms can only displace along basal planes, and that the S atoms are "squeezed out" along the c axis as a consequence of strain present in the Ta layers. The c displacement of the S atoms is therefore 90° out of phase with respect to their basal displacement. The basal displacements of the Ta and S atoms are arbitrarily phase shifted by means of an adjustable parame-

ter φ_x. A total of four parameters were used: longitudinal displacements for Ta, longitudinal and c displacements for S, and phase angle between basal displacements of Ta and S atoms. The theory developed by Giuliani and Overhauser[10] for polyatomic crystals was used to calculate diffracted intensities from displacements, after suitable extension was made to include the existence of several CDW's (three in our case). Since CDW satellites are weak, typically (2–3)% of Bragg reflections, extinction is believed to be absent. Using this model, with PTF included, we were able to fit at all temperatures, between 90° and 150 °C, all six CDW satellites with an R factor[11] between 0.012 and 0.024. All four parameters were found to be approximately constant, and the phason temperature factor was e^{-CT} with $C = 1.8\times10^{-3}$ K^{-1}. This factor, squared, multiplies the intensities of all first-order satellites. At 90 °C it is equal to 0.27, and decreases to 0.22 at 150 °C. For higher-order satellites it is even more important, since C must be multiplied by $(n_1^2+n_2^2+n_3^2)$, where n_1, n_2, and n_3 are the components of the scattering vectors in terms of the first-order satellite wave vectors. The most sensitive parameter was found to be the Ta displacement, $A_T \simeq 0.166\pm0.001$ Å. This value is in line with the value quoted by Moret and Colella[12] (0.23 Å) found by noting the first zero of a Bessel function $J_0(\vec{K}\cdot\vec{A}_i)$ affecting the Bragg reflections at room temperature, in the quasicommensurate phase. It is shown in Ref. 12 that the displacement should in fact *decrease* above 80 °C. The S basal displacement in our fittings turns out to be negligible, the S displacement along the c axis is 0.7–0.8 Å, and the phase angle φ_x, in excess of the "natural" phase associated with the crystallographic locations of Ta and S atoms, is about 56°. Another value for the displacement of Ta atoms with which we can compare is that found by Brouwer and Jellinek[13] using crystallographic methods: 0.25 Å, almost perpendicular to the c axis, again, at room temperature.

The general problem of thermal exciations in crystals with CDW's has been recently treated by Axe[14] using a different approach from that used by Overhauser. Axe's method is based on a phenomenological Landau theory and consists in expanding the free energy in terms of normal coordinates. A phason temperature factor was derived in this framework, which also shows the characteristic absence of a K^2 dependence, but there is no correction for first-order satellites.

This is contradicted by our experimental results. If the phason temperature factor is omitted, the fit is much worse ($R = 0.10$–0.12) and the Ta displacement values are unrealistically small: $\simeq 0.1$ Å. We convinced ourselves that the displacement values obtained by fitting without PTF were unacceptable when we used those values to calculate the intensity of a second-order satellite for which the intensity was measured. This was the $(0\bar{1}1)$ in rhombohedral indices, associated to the (030) Bragg reflection, located on the $(hk0)$ plane. Its integrated intensity was extremely weak and barely measureable: 4.5×10^{-9}. The calculated intensity with PTF was somewhat larger, about 35%. But if the PTF is ignored (set equal to 1), the calculated intensity becomes 13 times too big!

We then conclude that a phason temperature factor must be introduced in the theory when CDW satellites intensities are calculated from displacement values, and vice versa.

In view of this conclusion we believe that a lot of work that has been done on crystals with charge-density waves should be revised by taking into account the existence of phase excitations.

One may wonder how Brouwer and Jellinek[13] could get reasonable values for the displacements in TaS_2 without using the notion of a PTF. The point is that in a standard crystallographic determination all intensities are relative. No Bragg reflections were used in the refinement, so that the existence of a PTF was missed simply because, being K^2 independent, it was a constant multiplicative factor affecting *all reflections* included in the refinement. The importance of measuring absolute intensities in this kind of study appears obvious. Several other interesting aspects of this research, such as the behavior of higher-order satellites in the quasicommensurate and incommensurate phases, and the temperature dependence of the c components of the displacements, will be described in a more detailed forthcoming paper.

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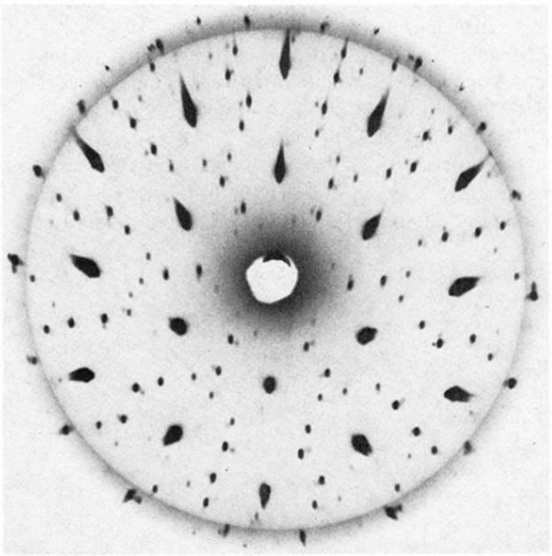

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