Temperature Dependence of the Orthorhombic Charge-Density-Wave Parameters in $2H$-TaSe$_2$ by ^{77}Se Nuclear Magnetic Resonance

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NMR spectra from $2H$-TaSe$_2$ are analyzed to obtain charge-density-wave parameters versus temperature. It is shown that there is a major orthorhombic distortion within each Se-Ta-Se layer, implying unexpectedly strong interlayer coupling. Evidence is also given for the existence of a significant interaction between discommensurations and the bulk charge-density wave, and an estimate of the width of a discommensuration is derived.

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The layered compound $2H$-TaSe$_2$ has been given much recent attention as a model two-dimensional charge-density-wave (CDW) material, where the CDW effect takes place in the Ta $5d$ conduction bands.[1] The associated periodic lattice distortion has been studied by electron,[1] neutron,[2] and x-ray[3] diffraction techniques, confirming the presence of an incommensurate CDW below 120 K and a commensurate phase below 90 K. NMR experiments[4,5] on ^{77}Se, which probe local charge modulation at the Se sites directly, have given results consistent with the earlier diffraction work, and have provided useful insights into the nature of the incommensurate phase.[5] The foregoing experiments were interpreted in terms of hexagonal CDW symmetry. Recently, however, Fung *et al.*[6] have reported convergent-beam electron diffraction data on $2H$-TaSe$_2$ characteristic of orthorhombic symmetry, a possibility discussed by Walker and Jacobs.[7]

Here, we report ^{77}Se NMR spectra[8] which provide the first detailed parametrization of the CDW state as a function of temperature. Our data are analyzed to yield the amplitude and phase parameters of the sinusoidal CDW first given by Walker and Jacobs.[9] From this analysis we conclude that the orthorhombic distortion from hexagonal symmetry is a major effect within each Se-Ta-Se layer. Our results explicitly rule out the displacement of two hexagonal CDW's within the unit cell as an explanantion for the data of Fung *et al.*[6] We find a total of twelve sets of fitting parameters, which are related to one another by Se atom site permutations. Eight of these solutions are comparatively moderate distortions from hexagonal symmetry; however, the remaining four describe a nominally one-dimensional CDW. This possibility is also supported by recent transmission-electron-microscopy work of Gibson, Chen, and McDonald.[10]

The ^{77}Se pulsed NMR study was conducted at 57 MHz with a sample of ~70 single-crystal $2H$-TaSe$_2$ platelets, each 50 μm thick, stacked so as to have a common c axis aligned parallel to the magnetic field. Representative spectra in Fig. 1 taken on warming reveal the following: (1) at least four spectral components, the two at the left being only partially resolved; (2) a surprising variation with temperature within the commensurate region and near the commensurate-to-incommensurate transition (CIT) (note the reversal in peak amplitude between 60 and 80 K which is rapidly retraced again above the CIT at 90 K); and (3) evidence at 110 K for satellite lines to the left of the main features, which we attribute to Se sites in domain walls. The commensurate spectra are clearly *not* consistent with the 3:3:3 distribution expected for hexagonal symmetry.[5,9] Further, no abrupt change is found between 30 and 60 K as has been suggested.[5]

In fitting our data we assume a linear and local relationship between CDW amplitude and the NMR shift K_i at Se site i. Band-structure calculations[11] show that the amount of chalcogen s character at the Fermi surface is negligibly small, implying that s-contact NMR shifts[5] are unimportant and that the primary shift mechanism is Van Vleck orbital magnetism. This is allowed at the Se sites by hybridization[11] of the Se $4p$ states into the Ta $5d$ conduction band. Although difficult to calculate, orbital shifts are thought in many cases to be a local, atomic property and to vary roughly as $K_i \propto n_i(N-n_i)$ for a partly filled band of N electron states per atom,[12] where n_i is the band occupation at site i. In this case a small change in n_i leads to a linear response in K_i. Covalency effects on K_i from neighboring Ta CDW amplitudes would alter the analysis only slightly.

We extract CDW parameters from the observed spectra by fitting line positions $\delta\rho_i$ in dimensionless NMR shift units by the expression from Ref. 9, where the origin is at a Ta site:

$$\delta\rho_i = \delta\rho + \delta\rho_{qi} + \rho_1 \cos(\vec{G}_1 \cdot \vec{r}_i/3 + \varphi_1) + \rho_2[\cos(\vec{G}_2 \cdot \vec{r}_i/3 + \varphi_2) + \cos(\vec{G}_3 \cdot \vec{r}_i/3 + \varphi_2)]. \quad (1)$$

Here $\delta\rho$ is the overall position parameter and $\delta\rho_{qi}$ is a small quadratic term which we find to be necessary in order to achieve high-quality fits. The $\vec{G}_\alpha$ are reciprocal-lattice vectors and ρ_1, ρ_2 and φ_1, φ_2 are amplitude and phase parameters, respectively. Equation (1) has orthohombic symmetry; the nine Se sites in the unit cell divide into three lines of weight 2 and three of weight 1. To discuss the quadratic term we introduce the notation $\delta\rho_{0i} = \rho_1 C_{1i} + \rho_2 C_{2i} + \rho_2 C_{3i}$ for the linear part of Eq. (1). Three single-parameter trial forms for the quadratic term were selected:

$$\delta\rho_{q\,\alpha i} = \alpha(\delta\rho_{0i})^2 = \alpha(\rho_1 C_{1i} + \rho_2 C_{2i} + \rho_2 C_{3i})^2, \quad (2)$$

$$\delta\rho_{q\,\beta i} = \beta(\rho_1{}^2 C_{1i}{}^2 + \rho_2{}^2 C_{2i}{}^2 + \rho_2{}^2 C_{3i}{}^2), \quad (3)$$

$$\delta\rho_{q\,\gamma i} = 2\gamma(\rho_1\rho_2 C_{1i} C_{2i} + \rho_1\rho_2 C_{1i} C_{3i} + \rho_2{}^2 C_{2i} C_{3i}). \quad (4)$$

These represent, respectively, a simple square of local density, squared terms only, and cross terms only. Combining Eq. (1) and one of Eqs. (2)-(4) yields six parameters to be determined in fitting the data.

Considering the α case [Eq. (2)] first, the fitting proceeded by assuming three Gaussian lines of amplitude 2 and three of amplitude 1, all with fixed linewidth obtained from the normal-state ^{77}Se resonance line shown at the bottom of Fig. 1. Figure 2 shows three typical least-squares fits to the experimental spectra. The fits are as good

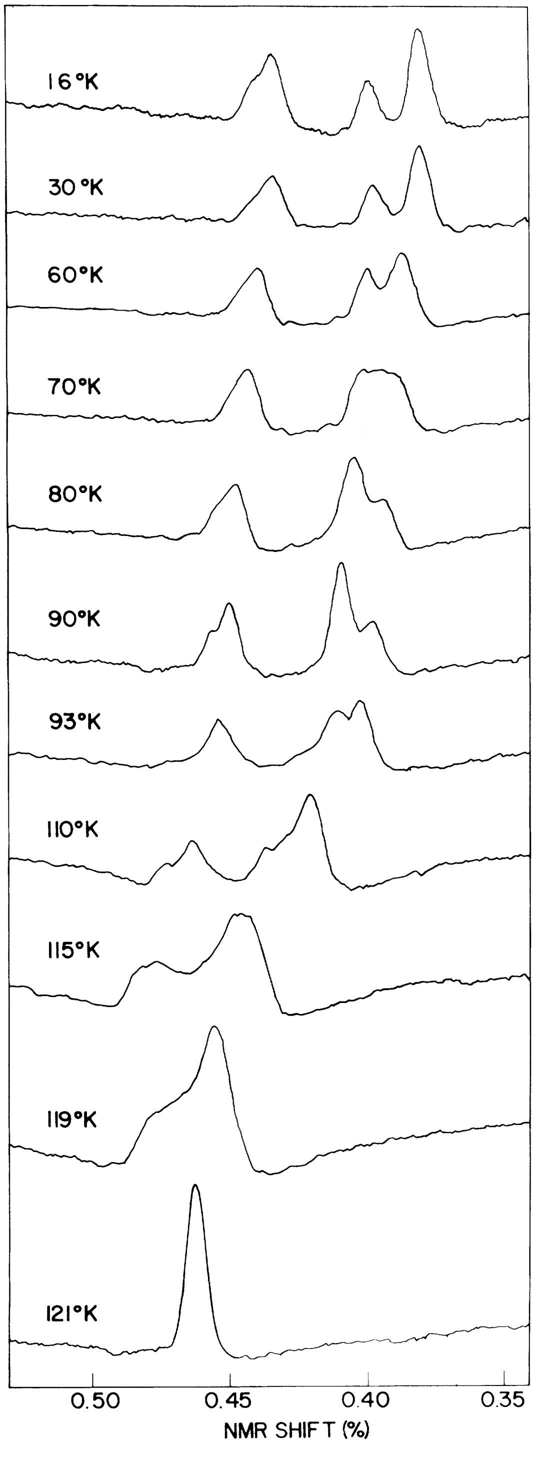

FIG. 1. Representative ^{77}Se pulsed NMR spectra, with field increasing to the right. NMR shifts are given relative to $\gamma/2\pi = 0.8118$ kHz/G.

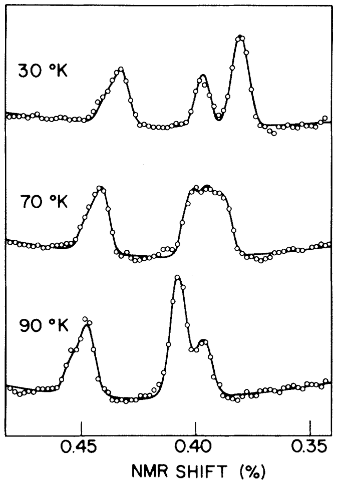

FIG. 2. Examples of least-squares computer fits to the NMR data at several temperatures.

as if the six line positions were independently adjustable. Allowing the linewidth parameter to vary freely made no significant further improvement.

In fitting the data our equations have been found to exhibit multiple solutions which arise in making a correspondence between the Se sites and the six line positions of the observed spectrum. Only the sequence (from left) 122211 has been found to yield a fit. Permutations within this sequence give $(3!)^2$ possible combinations. Trivial translations of origin reduce this by a factor of 3, leaving twelve distinct solutions. A computer search for these solutions was undertaken by scanning the $(\rho_1, \rho_2, \varphi_1, \varphi_2, \alpha)$ parameter space for the 90-K experimental line positions. This procedure found two complete sets of twelve site-permuted solutions, one with small quadratic terms and the other with quadratic terms comparable in size to the linear terms. The latter set is presumably unphysical. No other solutions were found.

Similar scans of parameter space at 90 K were conducted for the β and γ cases of Eqs. (3) and (4). In the β case no solutions of any kind were found, but in the γ case twelve solutions were again found, with values of ρ_1, ρ_2 and φ_1, φ_2 nearly equal to those found in the α case. The values of γ and α are each constant for the twelve solutions to which they correspond.[13] These coefficients varied only slightly with temperature, allowing fits of essentially equivalent quality to be obtained by fixing them to their mean value for all temperatures. The ratio γ/α is found to be 1.10. Thus, the cross terms have similar weight in both sets of fits and are clearly the more important element. This suggests that the CDW nonlinearity arises from interference between pairs of plane waves with different reciprocal-lattice vectors.

The parameters for the α fit are shown as a function of temperature in Fig. 3. Note that there are six pairs of nearly identical values, numbered 1–6 in the figure. Of these, four are two sets of solutions and their mirror images when reflected through a line of Se atoms transverse to $\vec{G}_1$. These solutions describe a CDW having $\rho_1 \approx \rho_2$. The two remaining pairs are the one-dimensional CDW solutions referred to above, having $\rho_1 \gg \rho_2$. Sudden changes in the temperature derivatives of the parameters set in above 90 K, indicating a strong interaction between discommensurations[14] and the bulk CDW properties. This is unexpected in existing theories.

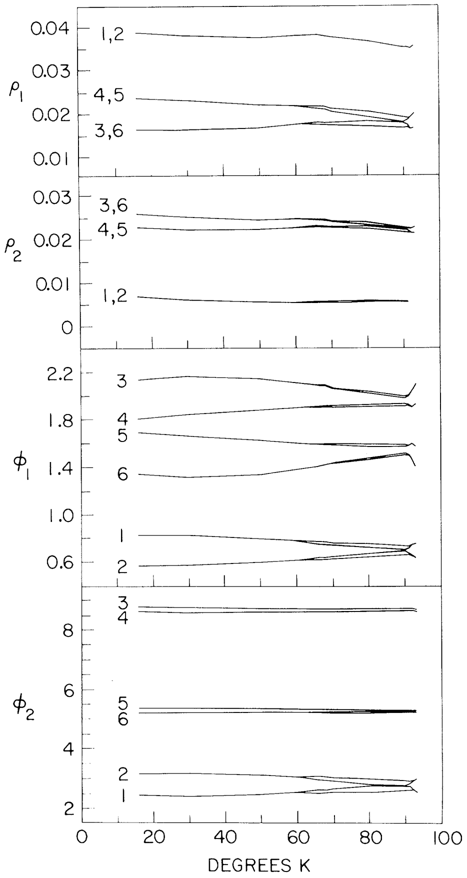

FIG. 3. Temperature dependence of the twelve sets of parameter values obtained using Eqs. (1) and (2). The twelve solutions occur in nearly degenerate pairs which are labeled 1–6 in the figure. For all fits at all temperatures $\alpha = 7.27$.

Another unexpected feature of the incommensurate phase is the occurrence of satellite lines. These are visible, though unresolved, at 93 K (Fig. 1) and are clearly in evidence at 110 K on the high-frequency (left) side of the main lines. At 93 K they contain 5% to 10% of the total NMR intensity, and thus of sample volume. We believe that these satellites arise from Se sites located within discommensurations. Assuming $\delta \cong 0.006$ for the corresponding value of incommensurability,[3] we estimate that the width of a discommensuration is 25–50 Å. This estimate suggests that discommensurations do indeed possess a finite width, in accord with a recent model for the internal structure of a discommensuration by Littlewood and Rice.[15]

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Molecular Phases in a Lattice-Gas Model

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A model system is introduced that is meant to simulate classically the saturation of chemical forces in species that form binary molecules. It is given in the form of a lattice-gas Ising-type Hamiltonian with suitable many-body forces. The existence and the properties of two molecular phases, one solid and one fluid, are made evident with a transfer-matrix study of the one-dimensional case.

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One of the difficulties of modeling the statistical mechanics of real condensed systems is that molecular phases must be either assumed at the outset or else left out completely, as a proper quantum-mechanical treatment of the chemical bond and its saturation is well beyond present-day possibilities. In describing systems that have molecular as well as nonmolecular phases, the usual assumption of a two-body additive pair potential is clearly unsuitable, since the effective attractive potential between any two particles may range, say, from strong to weak depending upon the state of bonding of each particle. In this sense, the molecular phases are an essential product of many-body forces. It is, in principle, conceivable to attempt to set up a classical Hamiltonian with many-body forces that could simulate accurately the behavior of a real system, e.g., hydrogen. However, a realistic implementation of this program appears difficult with respect to both modeling the forces and carrying out the actual calculation. In view of this difficulty, it is meaningful to investigate simple models that contain some of the essential features of the problem.

In this Letter we discuss an instructive lattice-gas model that exhibits both "molecular" and "atomic" phases. The model Hamiltonian is

$$\mathcal{H} = -\tfrac{1}{2}J \sum_{ijkl} (1-c_i)c_j c_k (1-c_l) - \mu \sum_i c_i , \qquad (1)$$