Distinct commensurate charge-density-wave phases in the $2H$-$TaSe_2$ structure

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Analysis of a model free energy shows that three distinct commensurate phases can exist in a layer of a material having the $2H$-$TaSe_2$ structure. Recent experimental results show that two of these phases occur in $2H$-$TaSe_2$, with a transition between them at a temperature between 30 and 52 K.

The compound $2H$-$TaSe_2$ exhibits a fascinating variety of charge-density-wave states[1,2]: a fully commensurate phase below 90 K, a "striped" incommensurate phase between 90 and 112 K and a hexagonal incommensurate phase between 112 and 122 K. Recently, Suits *et al.*[3] have presented nuclear magnetic resonance (NMR) evidence that the phase angle of the charge-density wave (CDW) changes significantly at some temperature between 30 and 60 K, thus indicating a possible phase transition in the commensurate state in this temperature range.

This article investigates the different commensurate states allowed by the phenomenological theory of Jacobs and Walker[4]; we find that there are three distinct commensurate states (called types I, II, and III). The type-I state has been discussed previously in the literature and is the only one consistent with the structure-factor measurements[1] on the commensurate phase of $2H$-$TaSe_2$ at 5 K. Recent unpublished results[5,6] on the same material at temperatures greater than 30 K are, however, inconsistent with the type-I phase. Our analysis shows that the presently available experimental data[1,3,5,6] are consistent with a phase transition from a low-temperature, type-I phase to a high-temperature, type-II phase.

The Landau theory of our previous article[4] is an extension of work of McMillan[7] and expresses the free energy in terms of order parameters ψ_j ($j=1, 2, 3$); from these, the departure of the charge density from its normal-state value can be obtained [Eq. (2.3) of Ref. 4]. We use this Landau theory to investigate commensurate states described by order parameters of the form $\psi_j = a\exp(i\phi_j)$, where a and the ϕ_j are real and independent of position. Minimization of the free energy F [Eq. (2.8) of Ref. 4] with respect to the phases ϕ_j shows that these quantities must have the form $\phi_j = \frac{2}{3}\pi n_j + \theta$, where the n_j are integers and θ is to be determined. Writing $n_1+n_2+n_3 = 3k+l$, where $l=0$, 1, or -1, and minimizing the free energy with respect to θ, we find the minimum to be

$$F = 3(A+B\delta^2)a^2 + 3(G+K)a^4 + 6|M|a^4\cos(-\tfrac{2}{3}\pi l + \phi_M) - 2a^3[|D|^2 + 6|DE|\cos(\tfrac{2}{3}\pi l + \phi_D - \phi_E) + 9|E|^2]^{1/2} \quad (1)$$

where the complex coefficients D, E, and M have been written $D = |D|\exp(i\phi_D)$, etc. It remains to minimize Eq. (1) with respect to a and l; explicit values of the parameters are required to accomplish this.

If $\phi_D = \phi_E = 0$ and $\phi_M = \pi$, as in Nakanishi and Shiba's analysis[8] of McMillan's free energy, the angle θ is zero and the minimum is obtained for $l=0$. Numerical work is required to minimize the more general form of Eq. (1), but one can easily see that the parameters can be chosen so that any one of the states $l=0$, 1 or -1 gives the minimum.

The states $l=0$, 1, and -1 (called the type-I, type-II, and type-III commensurate states, respectively) are shown in Fig. 1, where we have arbitrarily chosen θ to be roughly 20°. Clearly the threefold rotation axes for the three phases are in different positions (through Ta sites, unoccupied interstitial sites, and Se sites in the three cases).

The different symmetries of the three states mean that NMR and Mössbauer measurements can help to determine the structure. In the type-I, -II, and -III phases, there are, respectively, 3, 3, and 4 inequivalent Se sites with relative populations 1:1:1, 1:1:1, and 1:1:1:6; the relative populations of the Ta sites are 1:1:1:6, 1:1:1, and 1:1:1 in the three phases, respectively.

The experimental results on $2H$-$TaSe_2$ are the following. The ^{77}Se NMR results of Suits *et al.*[3] at all temperatures between 5 and 90 K are consistent with

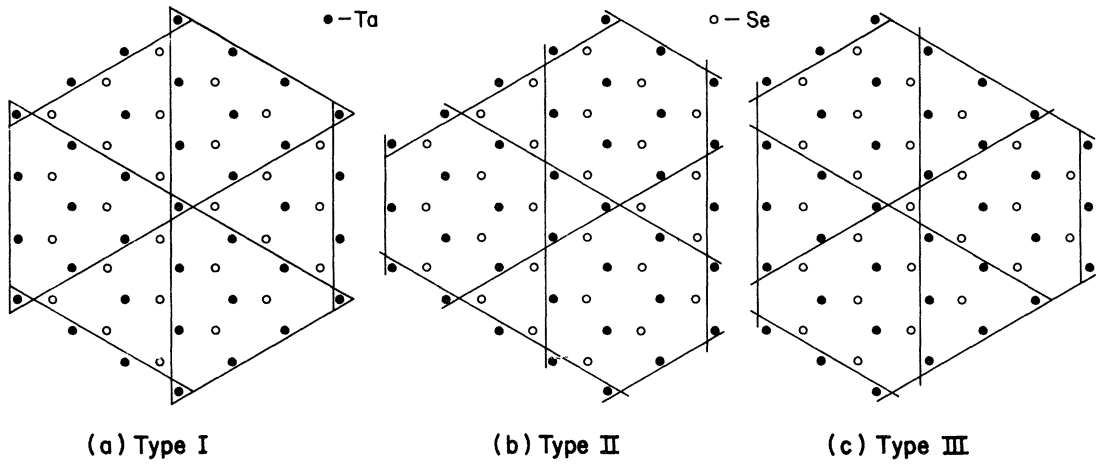

FIG. 1. Type-I, type-II, and type-III commensurate phases of a single layer of the $2H$-$TaSe_2$ structure. The ionic positions are projected onto a plane parallel to the layer. The solid lines represent the positions of the maxima of the three charge-density waves.

either type-I or type-II phases but not with the type-III phase; they observe three lines of equal intensity. The ^{181}Ta Mössbauer spectrum at 52 K, as measured by Pfeiffer,[5] is not consistent with the type-I phase but is consistent with types II and III. The neutron measurements at 5 K (Ref. 1) are consistent only with the type-I phase, in which the threefold axis is through a Ta site (see Fig. 1). We show below that the electron-diffraction experiments of the Bristol group[6] (at a temperature of roughly 30 K) are consistent with a type-II phase but not with a type-I phase. There must therefore be a phase transition (in general, first-order) between the low-temperature type-I phase and the high-temperature type-II phase. The apparent discontinuity in the CDW phase angle[3] is consistent with such a transition, but a reinterpretation of the results of Ref. 3 for this angle is necessary for the type-II phase. A first-order transition (with a small discontinuity in the amplitude of the order parameter) is consistent with both the temperature-dependence of the Knight shift[3] and some trial calculations which we have performed with Eq. (1).

Our theory is for a single layer of the $2H$-$TaSe_2$ structure and neglects the interlayer coupling terms which determine the stacking of the layers. We investigate the possible three-dimensional structures by assuming a center of symmetry (midway between two layers, on a line perpendicular to the layers and joining two Ta ions) and two layers per unit cell. Then the structure can be specified by specifying the structure of a single layer and the Ta sites between which the inversion center lies. Because the type-III phase is ruled out by the NMR measurements,[3] we discuss only structures based on the type-I and type-II phases.

In Fig. 2, we show one of the three distinct structures obtained by combining (in the manner described in the previous paragraph) two type-II layers with a given θ; shown are the CDW maxima and the normal-phase ionic positions in the conventional unit cell — we do not show the ionic displacements (which merely reflect the symmetry of the CDW). All three structures are orthorhombic. The electron-diffraction experiments of the Bristol group[6] on $2H$-$TaSe_2$ at a temperature of roughly 30 K give an orthorhombic structure with space group either $CmCm$ (No. 63 in the International Tables[9]) or $Cmc2_1$ (No. 36); there are two layers per unit cell. Following our discussion with Steeds, we determined that the above three structures all belong to the space group $CmCm$.

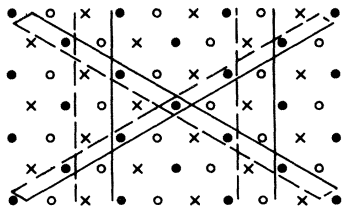

FIG. 2. Conventional orthorhombic unit cell of a commensurate CDW phase of $2H$-$TaSe_2$ containing two type-II layers. The Ta positions, Se positions, and CDW maxima for one layer are represented by filled circles, open circles, and solid lines, respectively, and, for the other layer, by filled circles, crosses, and dashed lines. All positions are projected onto a plane parallel to the layers; the ions are shown in their undistorted (normal-phase) positions.

The structures obtained by combining two type-I layers are not consistent with the electron-diffraction experiments described above. A structure having the hexagonal space group $P6_3/mmc$ (No. 194, the same as the normal phase) and having the symmetry of the phase measured at 5 K by Moncton *et al.*[1] is obtained by assuming an inversion center on a line through the central Ta ion in Fig. 1. Using different inversion centers, we obtain structures which are neither hexagonal nor orthorhombic.

In conclusion, we have shown that the Landau theory of our previous article[4] allows three different possibilities for the commensurate state of a layer of a material having the $2H$-$TaSe_2$ structure; of these, only the type-I structure has been described previously. There is strong experimental evidence that both the type-I and type-II phases occur in $2H$-$TaSe_2$, and that a phase transition between the two occurs at some temperature between 30 and 52 K.

There is a need for further experimental studies of the structure of the commensurate phases of $2H$-$TaSe_2$ at a variety of temperatures and pressures. It would be especially interesting to have more detailed information on the commensurate phase at high pressure.[10] On the theoretical side, there is need for a more detailed study of the stacking of the layers (by including interlayer interaction terms in the free energy); other problems are the determination of the value of θ in the two commensurate phases, and the determination of the displacements of the ions.

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