wave function contains bound and continuum terms. Thus the expression for the transition rate contains cross terms in addition to the exciton and the interband direct terms. The interband term describes the emission level in the CIS's under the exciton doublet. The cross terms, which may be called interference terms, can be negative and their maximum strength does not have to occur at the same $h\nu$ value as that for the exciton term. One would expect the interference terms to be weak; however when the exciton is polarization "forbidden" the magnitudes of the direct and interference terms could be comparable. Thus, the combination of the exciton and interference terms could give peaks differing in position and amplitude as observed in the data. Further, the narrow width of the enhancement lines is more consistent with an exciton model than a density-of-states model.

In conclusion we have presented a number of observed properties for the photoemission enhancement at the core to surface-state edge and suggested how they all may be understood with an excitonic model. Our results suggest that the exciton is small; that is, the Frenkel picture is more appropriate than the Wannier picture.

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New Mechanism for a Charge-Density-Wave Instability

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It is shown that a two-dimensional energy band with saddle points at the Fermi energy is unstable against charge density wave formation. The distorted phase is metallic with only a relatively small area of Fermi surface truncated at the saddle points. It is suggested that this model applies to the layer compounds $2H$-$TaSe_2$, $2H$-TaS_2, $2H$-$NbSe_2$, and 4Hb-TaS_2.

Lomer[1] first pointed out that a band structure in which electron and hole surfaces "nest" can favor the formation of a superlattice instability.[2] In this Letter we show that in a two-dimensional band structure a superlattice instability can arise in a model which does not have "nesting" in the usual sense. In this model large areas of Fermi surface are not truncated and indeed the low-temperature state may well be a better metal than the high-temperature phase. We suggest that this model applies to the $2H$-polytype layer compounds where charge-density waves (CDW) have recently been discovered.[3-7] There is a striking contrast between the effects of the CDW transition on the

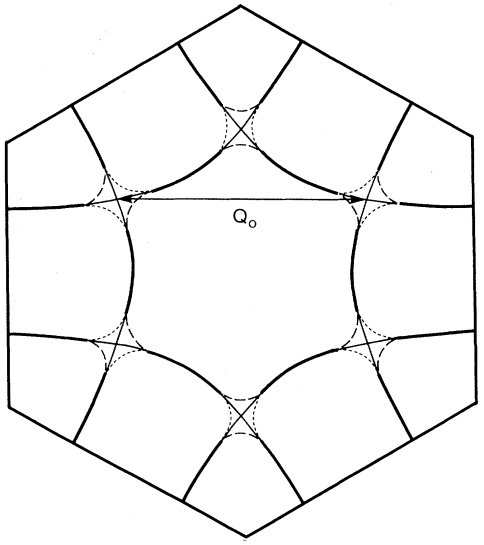

FIG. 1. A schematic view of Fermi surface in the basal plan of $2H$-$NbSe_2$ (after Mattheiss, Ref. 8, and Wilson, DiSalvo, and Mahajan, Ref. 6). The central portion is holelike. The solid line is the choice $\mu = 0$, the dashed line $\mu > 0$, and the dotted line $\mu < 0$.

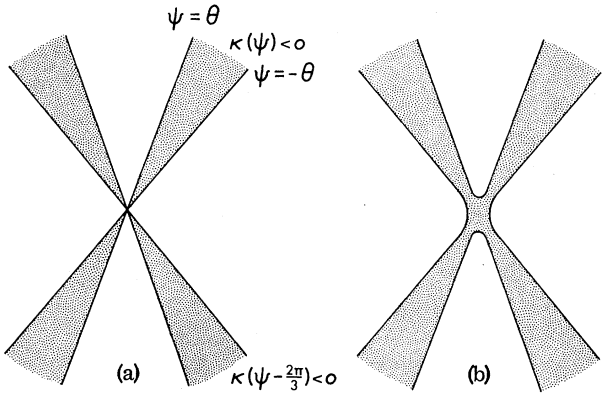

FIG. 2. (a) An expanded view of the saddle point at $\vec{k} = -\vec{Q}_0$ superposed on the saddle point at $\vec{k} = 0$. The joint surface enters in the evaluation of Eq. (2). The chemical potential $\mu = 0$ and $\theta = \pi/12$. The shaded area represents the occupied region of $\vec{k}$ space where (i) $\epsilon(\vec{k}) < 0$ $[\kappa(\psi) < 0]$ and (ii) $\epsilon(\vec{k} + Q_0) < 0$ $[\kappa(\psi - 2\pi/3) < 0]$. (b) The modifications introduced in the Fermi surface by the CDW.

conductivity and the magnetic susceptibility in the $2H$ polytypes and the $1T$ polytypes.[6] In the latter case the low-temperature phases are poor conductors and a "nesting" model should apply. $2H$-$NbSe_2$ and $2H$-$TaSe_2$ are better conductors in the presence of the CDW. A requirement of our model is a large and temperature-dependent density of states, such as that observed in $2H$-$NbSe_2$ and $2H$-$TaSe_2$.

The starting point for our model is the Fermi surface of $2H$-TaS_2 shown in Fig. 37 of Wilson, DiSalvo, and Mahajan[6] which was derived from calculations by Mattheiss.[8] The Fermi surface that we will assume is shown schematically in Fig. 1. The feature of interest is the occurrence of a saddle point in the d band at a set of six points. In the vicinity of a saddle point the energy band may be expanded in polar coordinates as

$$\epsilon_{\vec{k}} - \mu = (k^2/2m^*)(-\cos^2\psi + b^{-2}\sin^2\psi) - \mu \equiv (k^2/2m^*)\kappa(\psi) - \mu, \quad (1)$$

where we have taken a strictly two-dimensional band structure and $\vec{k}$ is measured from the saddle point. If accidentally the chemical potential μ is 0, then the Fermi surface consists of two intersecting straight lines. If $\mu > 0$ or $\mu < 0$ it has a hyperbolic form as shown in Fig. 1. The key quantity in a theory of CDW instabilities is the wave-vector–dependent susceptibility $\chi_0(\vec{Q})$ defined as

$$\chi_0(\vec{Q}) = \sum_{\vec{k},\sigma} \frac{f(\epsilon_{\vec{k}}) - f(\epsilon_{\vec{k}+\vec{Q}})}{\epsilon_{\vec{k}+\vec{Q}} - \epsilon_{\vec{k}}}, \quad (2)$$

where $f(\epsilon)$ is the Fermi function. At a wave vector $\vec{Q}_0$ connecting two saddle points[9] (see Fig. 1) the two surfaces $\epsilon_{\vec{k}+\vec{Q}} = \mu$ and $\epsilon_{\vec{k}} = \mu$ are hyperbolas rotated 120° with respect to each other [see Fig. 2(a)]. At $T = 0$°K and $\mu < 0$ one has

$$\chi_0(\vec{Q}_0;\mu) = \frac{4}{(2\pi)^2}\int_{\kappa(\psi)<0} \frac{d\psi}{\kappa(\psi - \frac{2}{3}\pi) - \kappa(\psi)} \int_{k(\psi)}^{k_0} \frac{k\,dk}{k^2/2m^*}, \quad (3)$$

where $k^2(\psi) = 2m^*|\mu/\kappa(\psi)|$ and the upper cutoff k_0 is approximately Q_1. Evaluating (3) leads to

$$\chi_0(\vec{Q}_0, \mu) = N_{Q_0}[\ln(\epsilon_0/|\mu|) + \text{const}], \quad (4)$$

where $N_{Q_0} = [2m^*/3^{1/2}\pi^2(1 + b^{-2})]\,D$ with $D = \ln|\tan(\pi/6 + \theta)/\tan(\pi/6 - \theta)|$, $\theta = \tan^{-1}b$, and $\epsilon_0 = k_0^2/2m^*$. The two surfaces in Fig. 2(a) in general do not nest. If $\theta = \pi/6$ or $\pi/3$ then there is nesting and N_{Q_0} diverges logarithmically and multiplies the logarithmic divergence in χ_0. Equation (4) applies for either sign of μ and gives a logarithmic divergence as $\mu \to 0$.[10] The divergence is localized in $\vec{Q}$ space around the value $\vec{Q}_0$ and χ_0 falls off logarithmically away from $\vec{Q}_0$. A similar divergence occurs for any choice of $\vec{Q}$ that connects two saddle points. The choice of $\vec{Q}$ in the CDW state depends in addition on a coupling constant whose strength is unknown.

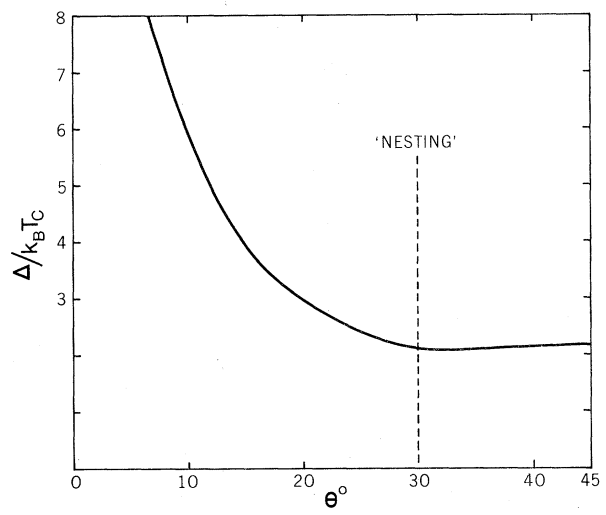

FIG. 3. The ratio Δ/kT_c from (8) as a function of θ. Note that our calculations do not apply at $\theta=\pi 6$ where the surfaces nest.

At a finite temperature $\chi_0(\vec{Q}_0)$ is never infinite but depends logarithmically on the ratio ϵ_0/k_BT for $k_BT \gg |\mu|$. A second-order transition to a CDW phase[11] occurs at a temperature T_c determined by

$$1=\lambda[D\ln(2\gamma\epsilon_0/\pi k_BT_c)+A(b)], \tag{5}$$

where $A(b)$ is an integral over ψ which depends only on b, and $\gamma=1.78$. The dimensionless coupling parameter λ can be viewed as incorporating electron-phonon and Coulomb interactions.[12]

For the present purposes we will restrict ourselves to a single CDW of wave vector $\vec{Q}_0$ and the energy bands in that case will be given by

$$E^{\alpha,\beta}(\vec{k})=\tfrac{1}{2}(\epsilon_{\vec{k}+\vec{Q}_0}+\epsilon_{\vec{k}}) \mp[\tfrac{1}{4}(\epsilon_{\vec{k}+\vec{Q}_0}-\epsilon_{\vec{k}})^2+\Delta^2]^{1/2}. \tag{6}$$

The energy-gap parameter Δ is determined by the gap equation which at $T=0$ and $\mu=0$ has the form

$$1=\lambda[D\ln(\epsilon_0/\Delta)+B(b)]. \tag{7}$$

Solving from (5) and (7) for the ratio Δ/k_BT_c we obtain

$$\Delta/kT_c=(\pi/2\gamma)\exp(B-A). \tag{8}$$

The exponent of (8) can be expressed as an angular integral and in Fig. 3 a plot is given of the ratio Δ/kT_c. Except for the limit of small b the ratio is roughly constant at a value ≈ 2.2 or 25% larger than the BCS value.

The energy bands in the CDW state are shown in Fig. 2(b). The Fermi surface is truncated only in the vicinity of the saddle points. Thus there is very little change in the area of the Fermi surface. The density of states $D_N(\epsilon)$ in the normal phase per saddle point is

$$D_N(\epsilon)=\frac{m^*b}{\pi^2}\ln\left(\frac{4\epsilon_0}{(1+b^2)|\epsilon|}\right). \tag{9}$$

The divergence at $\epsilon=0$ arises from the saddle point.[13] This singularity in the density of states gives rise to a strongly temperature-dependent Pauli susceptibility

$$\chi(T)=(m^*b/\pi^2)\ln[8\gamma\epsilon_0/(1+b^2)\pi k_BT] \tag{10}$$

for $|\mu|\ll kT$. In the presence of the CDW the density of states at $\epsilon=0$ is finite, in contrast to perfectly "nesting" bands:

$$D_{\mathrm{CDW}}(0)=\frac{2m^*b}{\pi^2}[\ln(4\epsilon_0^2/\Delta^2b^2) + \ln|\sin(\pi/3+2\theta)\sin(\pi/3-2\theta)|]. \tag{11}$$

There are singularities in $D_{\mathrm{CDW}}(\epsilon)$ at $\epsilon=\pm\Delta$. If $\pi/6<\theta<\pi/3$ then $D_{\mathrm{CDW}}(\epsilon)$ has logarithmic infinities at $\epsilon=\pm\Delta$. The form of $D_{\mathrm{CDW}}(\epsilon)$ illustrates the mechanism of stabilization is a splitting of the singularity at $\epsilon=0$ and the removal of one part below the Fermi level.

The singularity in the density of states at $\epsilon=0$ in the normal phase occurs also in $\chi_0(\vec{q},\ \mu=0)$ for q small. The contribution to $\chi_0(\vec{q})$ from each saddle point is

$$\chi_0(\vec{q},\ \mu=0,\ T=0)=\frac{m^*b}{\pi^2}\ln\left|\frac{4k_0^2(1+b^2)^{-1}}{q_x^2-b^{-2}q_y^2}\right|. \tag{12}$$

When $\vec{q}$ is parallel to the asymptotic directions of the hyperbolas there is a singularity at finite $\vec{q}$; but at finite T, χ_0 has the form given in Eq. (10). This singularity will lead to an elastic constant for waves in that direction of the form $L+M\ln T$ and a phonon softening away from $\vec{q}=0$.

The model also predicts a phonon softening for $\vec{q}=\vec{Q}_0$. At a second-order transition, the condition (5) together with the form of $\mathrm{Im}\chi_0(Q_0,\omega)$ $[\sim N_a(\omega/k_BT)\ln(k_BT/\omega)]$ ensures that there is a phonon of zero energy at $\vec{q}=\vec{Q}_0$.[14]

So far we have discussed a strictly two-dimensional band structure with a single CDW. Before the model can be directly applied to the layered compounds two generalizations are required. One is the incorporation of the three CDW related by hexagonal symmetry and the second is the inclusion of a finite bandwidth in the c direction. For CDW with $\vec{Q}$ vectors perpendicular to

c the latter can be handled by averaging over $\mu(k_z)$. The values of $\mu(k_z)$ found by Mattheiss[8] varied in different approximations. The strongly temperature-dependent magnetic susceptibilities[6] in $2H$-TaS_2 and $2H$-$TaSe_2$ suggest that $|\mu|/kT_c \sim 1$ in these materials. In general a finite-strength interaction λ is required to stabilize a CDW in three dimensions. Note, however, that Wattamaniuk, Tidman, and Frindt[15] have now firmly established in $4Hb$-TaS_2 that propagation of electrons along the c axis occurs by tunneling between metallic trigonal layers through insulating octahedral layers. In this case a two-dimensional band structure will apply. (In $4Hb$-TaS_2 a CDW transition occurs at $T_c = 20$ K in the metallic layers.)

Although our model at present is too simple to describe the layer compounds in detail, several qualitative remarks can be made on the transport properties. First the portion of Fermi surface removed by the CDW is the saddle point where the Fermi velocity is very small and the density of states high. These saddle points act as scattering sinks in the high-temperature phase and their removal can enhance the conductivity. Secondly it is clear from Fig. 2 that the connectivity of the Fermi surface can change and thus account for reversal of sign of the Hall effect observed in $2H$-$NbSe_2$[16] and $4Hb$-TaS_2.[17]

In conclusion this model was developed to account for the low-temperature CDW transition in the trigonal prismatic layer compounds. For these transitions it would appear to give a better account of their properties than the usual "nesting" models. It is striking that the phenomenology of these transitions is very similar to that observed at the martensitic transition in the $A15$ compounds, V_3Si and Nb_3Sn.[18] Gorkov[19] has recently put forward a model to describe these transitions as a commensurate CDW transition arising from a one-dimensional or nesting band structure. These martensitic transitions are also characterized by anomalous behavior of the Pauli susceptibility and of the sound velocity in certain directions, and a drop in the resisitivity similar to the behavior discussed here. The $A15$ compounds are three-dimensional but it is clearly worthwhile to see if there are any almost two-dimensional saddle points near the Fermi level in these materials.

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