ing around $\Delta E = 0$. Figure 2 qualitatively reproduces this calculated response.

The frequencies of the calculated phonon dispersion in Fig. 3 are, as they must be, symmetrical in scans A and B, but the intensities are not. In our present interpretation the two measured "dispersion curves" shown in Fig. 1 are identical at small ζ since the bcc phonons are most strongly sampled. As ζ increases the bcc phonons broaden and merge with the excitations associated with the ω fluctuations. The average frequency of this broad band differs between scans A and B because of asymmetries in the inelastic structure factor for these ω-phase phonons.

Finally what can be said about the soft-mode hypothesis? The data summarized in Fig. 1, particularly scan B taken alone, show the behavior expected of a soft-phonon branch, with the ZB mode itself overdamped. But the present calculations show that it is reasonable to attribute this low-frequency scattering not to a genuine soft mode, i.e., an incipient lattice instability, but rather to the modulation of quasistatic short-range order by ordinary low-frequency long-wavelength sound waves. *It is clear that this effect can occur generally in other similar circumstances.* Concerning the bcc-ω phase transformation it seems that the soft-mode description is inappropriate in that the important premonitory fluctuations involved occur at much lower than phononlike frequencies and in fact appear essentially static in these experiments.

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Importance of Chemical Effects in Determining the Free-Electron-Like Band Structure of $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$

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It is shown that a three-band model (i.e., inclusion of $5d_{z^2}$, $6s$, and $6p_z$ states) for the linear Pt chains in $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$ is inappropriate for a description of the electronic structure. The chemical effects of the ligands force an s-d hybridization which is k independent and leads to free-electron-like bands within a basically tight-binding scheme. This results in an explanation of the band structure deduced experimentally. A highly simplified model is also presented to explain the partial occupancy ($\frac{5}{6}$ full) of the band.

There has been a great deal of recent interest both experimentally[1-3] and theoretically[1,2,4-6] in the properties of a group of mixed-valence platinum salts of which $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$ (KCP) has been the most extensively studied. A large number of properties of KCP show the behavior expected on the basis of one-dimensional physical models. For example, the Peierls distortion, which occurs only in one-dimensional systems, has been observed experimentally in KCP.[7,8]

It is clear that the relevant aspects of the electronic structure of KCP associated with the pseudo one-dimensional properties arise primarily from the chains of platinum atoms and that a one-dimensional band-structure calculation is appropriate.

The usual first-order approach to the band structure of transition metals, which involve rather localized d electrons, is the tight-binding model. Surprisingly, however, there is a large amount of experimental evidence[3,9,10] to indicate that the band structure of KCP is free-electron-like, yielding a parabolic band with an associated effective mass equal to that of a free electron. The argument has been advanced[6] that it might be possible to modify the cosine-like band obtained in the tight-binding method by including the overlap and that in this manner one might obtain a band which resembles a free-electron parabola. This has, however, not been demonstrated, and in fact as we will discuss is incorrect.

In the present Letter we show that an essentially free-electron band structure can indeed result from such a basically tight-binding approach if one takes proper account of the chemistry of the molecular building blocks of the material.

The one-dimensional band calculations reported below were carried out within the framework of extended Hückel theory.[11-13] This linear combination of atomic orbitals–molecular orbital method is in the spirit of the simple tight-binding model but is improved in two important respects. Firstly the method is not restricted to nearest-neighbor interactions and, secondly, the overlap integrals are explicitly included in the secular equations. $5d_{z^2}$, $6s$, and $6p_z$ atomic orbitals on platinum were included. The necessary orbital exponents and parameters for the method are shown in Table I and are essentially identical to those used previously to study a different problem in a related material.[13] Lattice sums were carried out to third-nearest neighbors. The observed Pt-Pt distance of 2.89 Å was used.

TABLE I. Orbital exponents (ξ in inverse bohrs) and ionization potentials (I in electron volts) used in the extended Hückel band-structure calculation (see Ref. 12).

Orbital	ξ	I
$5d$	3.00	10.61
$6s$	2.60	9.80
$6p$	2.45	5.35

In Fig. 1 we show the bands obtained in a three-band model using s, p_z, and d_{z^2} Bloch functions, the coefficients of which are determined by the solution of the secular equations. The band structure is very similar to a recent Korringa-Kohn-Rostoker band structure calculated by Whitmore.[14] This band structure, however, is inconsistent with several experimental observations. In particular there are no observed interband transitions of significant intensity in the energy region which would correspond to transitions between the two lowest bands of Fig. 1.

However, in obtaining Fig. 1 we have completely ignored the fact that each platinum atom in KCP is surrounded by four cyano groups and that they exert strong chemical forces in the $Pt(CN)_4^{--}$ molecular unit. Let us assume for the moment that the primary role of the ligands is to fix the s-d_{z^2} hybridization on the Pt. We can then carry out a two-band calculation in which the two basis functions are an s-d_{z^2} hybrid and a p_z Bloch orbital. Hence, we have assumed that the relative amounts of s and d are independent of k. The results of a calculation based on this assumption in which the hybrid is 84% d and 16% s are shown in Fig. 2 together with the free-electron parabolic band. The agreement is indeed striking. We have therefore succeeded, by including the proper chemistry, in reconciling the observed free-electron-like behavior of KCP with the intuitive
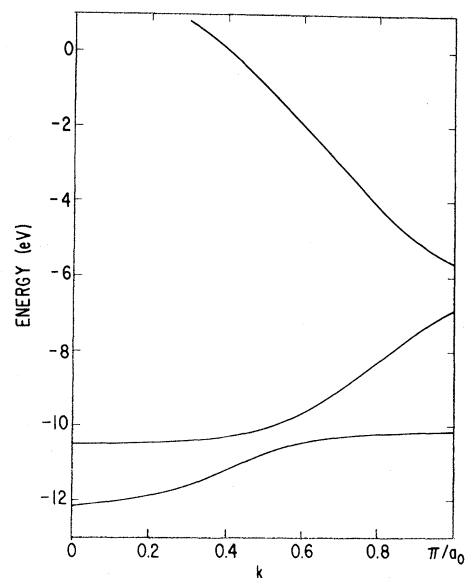

FIG. 1. Band structure obtained from a three-band model. The basis functions are $5d_{z^2}$, $6s$, and $6p_z$ Bloch functions.
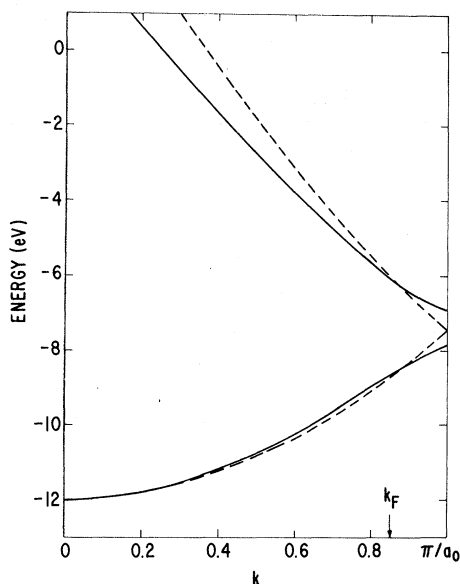
FIG. 2. Band structure obtained from a two-band model. The basis functions are a $5d_{z^2}-6s$ hybrid Bloch function (84% d, 16% s) and a $6p_z$ Bloch function. The dashed line is the free-electron $(m^* = m_e)$ parabolic band.

desire to be able to treat a d electron system within an essentially tight-binding scheme.

An analysis of the calculations has shown that parabolic bands do not result simply by including the overlap in a strictly tight-binding approach as has been suggested by Bloch and Weisman.[6] The parabolic band depends on three factors: proper hybridization, inclusion of overlap, and also some mixing with the p functions. If any one of these three factors is ignored the band departs from the free-electron parabola.

Hence, the above results depend crucially on the assumption of the same s-d mixing holding for all values of k. A posteriori the assumption is justified by the excellent agreement with experiment demonstrated above. However, chemical intuition would indicate a priori the validity of this assumption and indeed this can be demonstrated in a quantitative manner by reference to independent calculations on the molecular units. Interrante and Messmer[15] have performed self-consistent-field-$X\alpha$-standing-wave calculations on $Pt(CN)_4^{--}$ and $[Pt(CN)_4^{--}]_2$. If the above argument is valid then the molecular orbitals of the monomer and the dimer, which are predominantly d_{z^2} orbitals on Pt and thus are the precursors of the relevant one-dimensional bands, should all have a constant fractional d character. We

have performed a partial-wave analysis of these orbitals and have found the d orbital contributions to be 81%, 80%, and 84% for the three relevant orbitals. This is a convincing demonstration of the appropriateness of the above assumption.

Another major problem in this and related compounds is to understand why there is a fixed value for the partial oxidation of the Pt atoms. It is clear that this partial oxidation is responsible for the metallic behavior parallel to the chains and that a complete explanation of the stoichiometry of KCP is an extremely complex matter involving energy contributions from donor and acceptor as well as Madelung-like terms for the resulting charged species. None the less, if we are willing to oversimplify our considerations, perhaps some insight can be gained. In this light we will focus our attention on the Pt chain and regard the Br atoms simply as a charge sink which is capable of accepting as many electrons as the platinum atoms are willing to give up.

If we consider the bonding and antibonding combinations of d_{z^2} orbitals on two adjacent Pt atoms we recognize that a bonding stabilization (ΔE) equal to approximately one-half the energy splitting of the bonding and antibonding orbitals is obtained if we remove an electron from the latter. However, this electron removal leads to a repulsive interaction between the remaining positively charged Pt atoms. The amount of charge transfer will then depend on a balance between the stabilization gained by removing the electrons and the Coulomb repulsion between the charged species left behind. If the charge transferred is Q_t then the stabilization is $-2Q_t\Delta E$ and the repulsion is $+Q_t^2/R$. Taking ΔE (0.092 hartree = 2.5 eV) from the self-consistent-field-$X\alpha$-standing-wave calculations mentioned above and minimizing the sum of the two terms with respect to Q_t, we obtain an equilibrium value of Q_t equal to 0.25 which is reasonably close to the observed stoichiometry. While this treatment of the charge transfer is clearly highly simplified, it does lead to a pleasing intuitive picture which we feel accounts for the main physical effects involved.

Both of the models presented in this Letter, the band calculation and the treatment of charge transfer, emphasize the importance of molecular aspects of KCP. These ideas can undoubtedly be applied to other systems and in particular work is in progress on a treatment of the organic charge-transfer system tetrathiafulvalene tetra-

cyanoquinodimethane.

We are grateful to L. V. Interrante for useful discussions.

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Effect of the Surface Energy of Electron-Hole Drops on Their Luminescence Spectrum in Ge

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The size of small electron-hole drops near threshold is investigated in Ge using a small shift of their main luminescence line due to their surface energy σ. The smallest radii measured at different temperatures are compared with the minimum stable radii given by a model taking σ and the drop binding energy φ into account. We find an excellent agreement if we use the spectroscopic value of φ (23 K).

Experimental and theoretical investigations of electron-hole drops (EHD's) in Ge have received much attention during the last five years. Most of the work to date has been devoted to measuring and understanding bulk properties of this liquid phase.[1] However, different authors[2] have calculated recently the EHD surface energy σ which is $\sigma \sim 10^{-4}$ erg/cm² in Ge. This quantity has been also estimated from light-scattering measurements by Alekseev *et al.*[3] ($\sigma = 1.6 \times 10^{-4}$ erg/cm²) and by Silver[4] ($\sigma = 10^{-3}$ erg/cm²).

We report here experiments showing that for small EHD's their surface energy has an effect on their luminescence. Indeed, using a sensitive differential method, we have observed that the LA-phonon-assisted emission line of EHD's in Ge shifts towards high energy with decreasing excitation level (J) when it is not too far from the threshold J_{th} for EHD formation. This is explained by a change in the EHD chemical potential due to σ and provides a determination of the mean EHD radius. The temperature dependence of the smallest measured radii is in very good agreement with that of the minimum stable radii given by a

simple model which takes σ into account. This model allows us to get from our data the ratio A/σ, where A is the Richardson-Dushman constant. The agreement with the theoretical value of A/σ is satisfying if we use the spectroscopic value[5] of the EHD binding energy (23 K).

The idea of the experiments reported here is to measure near J_{th} the shift ΔE in the luminescence line of the EHD's when their size changes. As shown below, the size of EHD's depends on the pump level and also, because of hysteresis,[6] on the pump-level history. In these experiments, a pure Ge sample ($N_A - N_D \sim 2 \times 10^{10}$ cm⁻³) is immersed in liquid He and excited by a stable cw mercury or halogen lamp monitored with a special chopper as shown in Figs. 1(a) and 1(b), so that both levels of excitation J_1 and J_2, whose ratio was always equal to 10, have opposite phases. The corresponding luminescence lines, which are analyzed with a grating spectrometer followed by a PbS cell, are sent into a lock-in amplifier and are normalized by adjusting the duration of J_1 so that they have the same amplitude at their maximum. The resulting signal is thus pro-