

splitting of Gd in Ag should be extremely small⁸ it is unlikely that this behavior of the thermoelectric power results from crystalline field effects.

Further we notice that the sign of Q_1 , which depends on the ordinary scattering potential,² is negative. This implies that the Tb ion is more strongly screened than the La ion and is therefore effectively a negative (repulsive) scattering center.

In conclusion, we have demonstrated the existence of an anomaly in the thermoelectric power due to inelastic scattering of conduction electrons by the crystal-field-split impurity levels. Our results show that measurements of the thermoelectric power provide an interesting tool for investigating crystal field effects in metals.

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Band Structure of MoS₂ and NbS₂

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The simplified linear combination of muffin-tin orbitals method has been used to calculate the energy bands of MoS₂ and NbS₂. The calculated bands are in excellent agreement with photoemission data and provide a new interpretation of optical absorption spectra different from that of Wilson and Yoffe. The effect of the weak interlayer potential on the d_{z^2} conduction band is shown explicitly.

The simplified linear combination of muffin-tin orbitals method^{1,2} has been used to perform the first *ab initio* energy-band calculations on MoS₂ and NbS₂, two members of a large family of structurally and chemically similar layered transition metal dichalcogenides. These bands, which do not require empirical adjustment, offer the first consistent explanation of both the McMenamin and Spicer³ (MS) photoemission work on MoS₂ and the Wilson and Yoffe⁴ (WY) optical absorption spectra of MoS₂. The calculated d_{z^2} band in MoS₂ is about 2.7 eV wide, overlaps the S *p* bands, and is 1.1 eV below the *d/p* bands, in excellent agreement with MS. By assigning interband transitions between the d_{z^2} and *d/p* bands, we account for the main features of the WY optical absorption spectra. Our bands differ from the rigid-band model of WY who assumed the absorption spectra to result from *p-d/p* interband

transitions and the d_{z^2} band to be narrow, non-bonding, and located within the bonding-antibonding gap.

The layered transition-metal compounds are of particular interest because some members appear to exhibit "two-dimensional superconducting properties,"⁵ which can be changed by intercalating the layers with organic molecules. We present evidence that intercalation with organic molecules changes the shape of the Fermi surface and thus T_c . It is unlikely that organic molecules actually contribute electrons to the metallic d_{z^2} band.

The 2H-MoS₂ and 2H-NbS₂ structures are both formed from layers⁴ consisting of two close-packed sheets of S atoms with a sheet of metal atoms occupying trigonal prismatic sites between the S sheets. The octahedral sites between layers are empty, resulting in large open areas.

TABLE I. Comparison of theoretically expected absorption in MoS_2 with experiment.

	Experiment (eV)	Theory (eV)
<i>A</i>	1.910	1.91
<i>B</i>	2.112	2.11
<i>d</i>	2.63	Shoulder not identified
<i>C</i>	2.760	2.58
<i>D</i>	3.175	3.17
α	3.685	3.79
β	3.930	3.99
<i>E</i>	4.59	4.42
<i>F</i>	4.86	4.79
<i>A', B'</i>	Not observed	2.39

pected. The spectra are characterized at low energy by sharp excitonic transitions (e.g., *A, B*) on a relatively low absorption background. The broad absorption peaks (*C, D*) at higher energy are thought to be the result of strong interband absorption.⁴ Wilson and Yoffe concluded that the *A, B* peaks are a spin-orbit-split pair because of the size of the separation (0.20 eV) and because of the increase in the separation with molecular weight (0.26 eV in MoSe_2).

In Table I we compare the MoS_2 experimental interband energies of Fig. 2 with the assignments made in Fig. 1. The *A, B* exciton results from the 2.01-eV transition at the \bar{A} point. The A_1 level does not split under spin-orbit coupling so that a 0.2-eV splitting of the A_3 level gives rise to 1.91- and 2.11-eV transitions which are in perfect agreement with experiment.

Similar excitonic structures could be expected at \bar{H} . This structure (*A', B'*) should appear at about 2.39 eV which is between the *A, B* and *C, D* structures. This structure is not observed in MoS_2 probably because the transition probability at \bar{H} is too low for exciton formation. Comparison of the wave functions supports our hypothesis since the transition probability is lower at \bar{H} than at \bar{A} . We believe that the *A', B'* exciton structure observed in MoSe_2 and MoTe_2 ⁷ (not in Fig. 2 although very similar) results from the assigned *A', B'* transition at \bar{H} because the *p* content of the *d/p* bands increases with anion size.

The transition probabilities in MoS_2 are greater for the *C* and *D* transitions than for the *A, B* and *A', B'* transitions since the higher energy *d* states have a greater admixture of *S p* character. As a result, the absorption is stronger for the *C* and

D interband transitions. The *C* interband transition requires a 0.2-eV adjustment for agreement with experiment whereas the *D* transition needs no adjustment.

The α, β peaks are interpreted by Beal, Knights, and Liang⁷ to be spin-orbit-split structure. We assign this structure to the 3.89-eV transition at the \bar{A} point which is the first *p-d* transition. Spin orbit splitting should be small for the *p* state with a 0.2-eV splitting for the *d* state.

The *E* feature probably results from transitions at \bar{L} and the *F* feature from either \bar{L} or \bar{A} . A more accurate interpretation of the spectra requires a detailed joint density-of-states calculation. Without such a calculation we cannot be certain that some optical critical points were not overlooked.

Finally, we examine the effect of the unoccupied-site potentials on the band structure of NbS_2 in order to investigate intercalation effects. In Fig. 3, solid lines represent the band structure when all eight sites are included, whereas the dashed line represents only the d_{z^2} bands when the six filled sites are included. The Nb and S potentials are the same for both cases. In the six-atom case, the crystal is not neutral because the charge density in the layers is not included. However, we assume this has little effect on the bands.

Thus, from Fig. 3 we see that the d_{z^2} band is wider, and the overlap with the *p* bands is greater, when the layers are insulated from each other by a zero-potential region. The Fermi surface geometry also changes. Intercalation by organic molecules might narrow the conduction bands even more than our weak empty-site potentials. Further band calculations are required to determine whether organic molecules decrease the overlap of the *p* bands with the d_{z^2} conduction band and whether the density of states at E_F is increased by the resultant change in Fermi surface geometry. However, we do see that the Fermi surface can be changed without having the organic molecules donate electrons to the d_{z^2} band and this may account for the change in T_c with intercalation.⁵ Similar band effects are found in MoS_2 . Experimentally, the *A, B* exciton energy should shift upon intercalation.

In NbS_2 , the d_{z^2} band is half filled. Thus the Fermi energy should occur at about -8.0 eV, resulting in hole and electron surfaces. Temperature-dependent Hall coefficient measurements for NbS_2 indicate two types of carriers.⁸

Note added.—After submitting this paper for

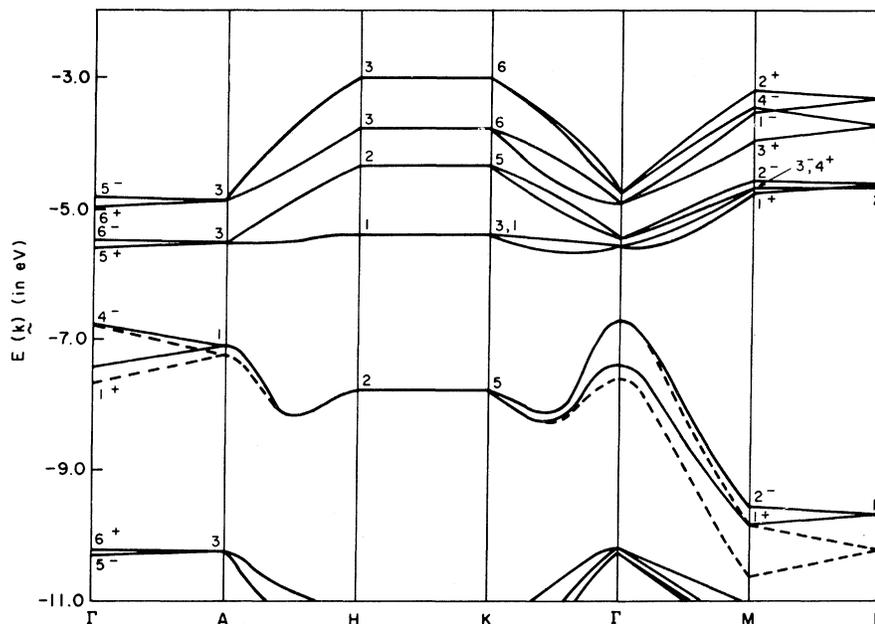


FIG. 3. Band structure of NbS_2 with interlayer region (solid line) and without interlayer region (dashed line represents only d_{z^2} band).

publication, we received L. F. Mattheiss's⁹ augmented plane-wave (APW) calculation of the energy bands in MoS_2 using a potential constructed from the same atomic charge densities that were used in our LCMTO calculation. The bands differ from ours and experiment in that the d_{z^2} band is too narrow (1.0 eV) and does not overlap the p bands. The optical absorption excitons are also not explained. Mattheiss attributes the lack of agreement with experiment to the approximate form of exchange used and to the lack of self-consistency in the potential. Our results show that it is the non-muffin-tin part of the potential that causes the d_{z^2} band to widen and overlap the p bands. We obtain bands similar to the APW work only if the non-muffin-tin part of potential is excluded.

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