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## High-Temperature Superconductivity in Bridge and Layer Compounds

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A microscopic model is presented for the structure and superconductivity of  $A_xT_{1+y}C_2$  compounds, where  $A$  is a monovalent atom or radical,  $T$  is an even-valence transition metal,  $C$  is a chalcogenide, and the parameters  $x$  and  $y$  lie in the ranges  $0.1 < x \lesssim 0.3$ ,  $0 \leq y \lesssim 0.5$ . The model explains why the maximum superconducting transition temperature  $T_S^{\text{max}}$  is higher than 12°K in bridge compounds with  $y = 0.1$ , although the maximum value of  $T_S$  observed in related layer compounds with  $y = 0.0$  is about 6°K.

Interest in layer compounds as possible superconductive materials was stimulated by the work of Wilson and Yoffe (WY)<sup>1</sup> on the transition-metal dichalcogenides  $TC_2$ . When these materials are pure and the even-valence transition metal  $T$  belongs to column IVb or VIb, they form sandwich structures which are small-gap semiconductors. In analogy with Cohen's many-valley superconductivity<sup>2</sup> in GeTe, WY suggested<sup>1</sup> that the  $TC_2$  semiconductors might become superconductive if properly doped, and that an easy way to achieve high carrier densities was through intercalation of monovalent atoms or radicals. Several column-Vb (odd-valence) transition-metal dichalcogenides were already known to be metallic and superconducting, and these have recently been intercalated<sup>3</sup> with the result that those with  $T_S$  near 1°K in the pure state may exhibit increased values of  $T_S$  up to 3°K when intercalated, while those with  $T_S$  near 6°K in the pure state actually show a decrease of  $T_S$  with intercalation.

The compound  $Ti_{1+y}S_2$  ( $0.1 \leq y \leq 0.5$ ) does not have a sandwich structure. The Ti atoms are distributed alternately between filled and partially occupied sheets, tending as  $y$  approaches 0.5 to the  $Ti_3S_4$  structure, where the metal layers are alternately filled and half filled.<sup>4</sup> The  $y$  or supernumary Ti atoms act as bridges connecting filled Ti sheets, and make a contribution to the density of states at the Fermi energy intrinsically different from that of intercalated donors. Barz *et al.*<sup>5</sup> have discovered that the value of  $T_S$  in intercalated  $Ti_{1+y}S_2$  is about 10 to 13°K, or about twice as great as  $T_S^{\text{max}}$  in the intercalated  $T(Vb)C_2$  family.<sup>3</sup> This suggests that the  $A_xT_{1+y}C_2$

compounds with  $y \gtrsim 0.1$  be described as intercalated bridge compounds in contrast to  $A_xTC_2$  compounds, which may be described simply as intercalation compounds. As we shall see, the experimental evidence<sup>5</sup> indicates that the role played by the intercalated  $A$  atoms in affecting  $T_S$  is incidental in the bridge compounds.

A semiempirical model of the energy bands of  $TC_2$  compounds has recently been presented.<sup>6</sup> The analysis suggests that stoichiometric  $TiS_2$  would have an energy gap of about 1 eV separating a filled Ti 3d-S 3p valence band from an empty Ti 4s conduction band. These two bands have a high, approximately two-dimensional, density of states, as shown in Fig. 1(a). When intercalated donors in sufficient density are added to the material, a low, broad, three-dimensional s-p band is expected to fill the energy gap of the host semiconductor. Because the intercalated ions

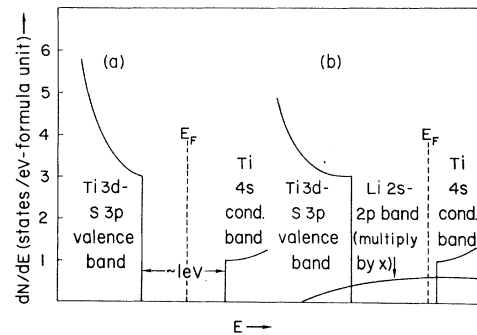


FIG. 1. Density of electronic states near  $E_F$  in stoichiometric  $TiS_2$ . (a) Without intercalation  $TiS_2$  is a small-gap sandwich semiconductor. (b)  $Li_xTiS_2$  ( $x \sim \frac{1}{2}$ ) is a metal with a low density of states near  $E_F$ .

act as donors, the Fermi energy may fall within 0.1 eV of the very high density of states at the bottom of the conduction band, as shown in Fig. 1(b). This could give rise to an enhancement of  $T_S$  by virtual scattering of electrons into conduction-band intermediate states. However, the low density of states at  $E_F$  would make  $\text{Li}_x\text{Ti}_{1.0}\text{S}_2$  basically similar to a dilute alkali metal, and superconductivity has yet to be observed in alkali metals at normal densities.

Microscopic models for the electronic density of states in bridge compounds are shown in Figs. 2(a) and 2(b), while the effects of intercalation can be obtained by combining either of these sketches with Fig. 1(b). In 2(a), which is drawn for values of  $y$  near 0.1, we assume that each bridge Ti atom is covalently bonded to one and only one Ti atom in a filled layer, at a distance 2.88 Å away,<sup>5</sup> compared to 2.90 Å in metallic Ti. The 3d states of the bridge Ti atoms are split into  $\sigma$ ,  $\pi$ , and  $\delta$  bonding and antibonding states through interaction with the 3d states of the Ti neighbor. The  $dd\delta$  overlap is assumed to be small ( $\approx 0.1$  eV), so that the effect of residual interactions broadens the  $d\delta$  and  $d\delta^*$  levels into a single band, which is approximately  $\frac{1}{4}$  full and 0.2 eV wide.

An alternate model for the energy levels of the bridge atoms includes their interaction with

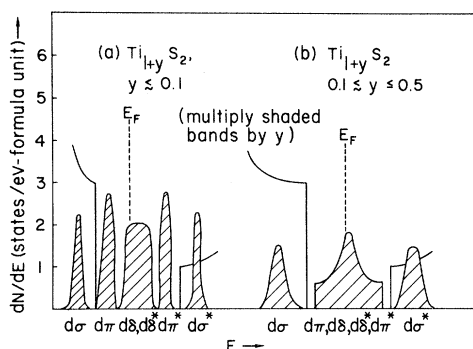


FIG. 2. Density of electronic states near  $E_F$  in  $\text{Ti}_{1+y}\text{S}_2$ . Because  $\text{Ti}_{1+y}\text{S}_2$  is a bridge compound, there is a high density of states near  $E_F$  associated with the supernumerary or bridge  $\text{Ti}_y$  atoms. The  $d$  states of the latter are labeled  $\sigma$ ,  $\pi$ , or  $\delta$ , according as  $m_z = 0, \pm 1$ , or  $\pm 2$ , where  $z$  is the axis normal to the  $\text{TiS}_2$  layers. (a) Only the  $\delta$  and  $\delta^*$  states are assumed to have merged to form a two-dimensional energy band. (b) The  $\delta$  and  $\pi$  bonding and antibonding states are assumed to have merged. In either case,  $E_F$  falls near the middle of the  $\text{TiS}_2$  energy gap, in a region of high density of states associated with the bridge atoms. The effect of intercalated Li atoms in  $\text{Li}_x\text{Ti}_{1+y}\text{S}_2$  on the density of states is similar to that shown in Fig. 1(b).

slightly more distant Ti atoms in filled layers. In this case, which is shown in Fig. 2(b), the  $d\pi$ ,  $d\delta$ ,  $d\delta^*$ , and  $d\pi^*$  levels form a two-dimensional energy band 0.5–1.0 eV wide. A high peak is found in the center of this band, the broadened remnant of the logarithmic singularity characteristic of two-dimensional energy bands. The Fermi energy falls on the low-energy shoulder of this peak.

The effects of intercalation with Li atoms are analogous to those shown in Fig. 1. The Li atoms add a low density of states ( $\sim 0.5$  electron/eV atom) in the gap region. Comparison with Fig. 1(b) shows that there is some charge transfer  $Qe$  from intercalated Li to bridge Ti atoms. The amount of this charge transfer is expected to be about the same so long as  $x \gtrsim y$ . Its magnitude  $Q$  can be estimated from Ramqvist's correlation of electronegativity differences with ESCA shifts<sup>7</sup> in transition-metal carbides, which gives  $Q = 0.2$ . This charge transfer shifts  $E_F$  slightly upward and increases  $dN(E_F)/dE$  somewhat.

For situations when  $dN(E_F)/dE$  is large (of order 10 electrons/eV atom), the systematics of the connection between  $dN(E_F)/dE$  and the effective electron-electron interaction parameter  $V$  are not well established. However, it is believed that very high values of  $dN(E_F)/dE$  give rise<sup>8</sup> to high values of  $T_S$ . Also soft lattice modes enhance  $T_S$ , and the bridge Ti atoms are relatively free to move within their partially filled sheet.

Evidence on motion of the bridge atoms is provided by the instability<sup>5</sup> of  $\text{Li}_x\text{Ti}_{1.1}\text{S}_2$  between 77 and 600°K. When the samples are held for a few hours at room temperature,  $T_S$  drops a few degrees and bulk superconductivity disappears. Subsequent annealing reverses the transition and restores the previous value of  $T_S > 10^\circ\text{K}$ . The simplest explanation for this behavior is to assume that the supernumerary Ti atoms condense either at grain boundaries or in regions of S deficiency, and that the intercalated Li ions lower the boiling point  $T_B$  of the two-dimensional supernumerary Ti atoms to the range  $300^\circ\text{K} < T_B < 600^\circ\text{K}$ . Thus the main function of the Li ions is to reduce  $T_B$  to a low enough value to permit "evaporation" of condensed supernumerary Ti atoms at or below the annealing temperature to form a two-dimensional Li-Ti gas in the partially filled sheets.

The foregoing discussion illustrates a general principle which may have considerable value in the search for new materials with high values of  $T_S$ . These new materials will probably be transi-

tion-metal compounds which are unstable at room temperature, but which can be prepared at high temperatures. Stability at high temperatures is promoted by entropy contributions to the free energy if the material is ternary or quaternary rather than binary. Here we use these terms in a structural sense and not a chemical one. For example, in  $\text{Li}_x\text{Ti}_{1+y}\text{S}_2$  compounds,  $\text{TiS}_2$  is one element, while  $\text{Li}_x$  and  $\text{Ti}_y$  are the second and third elements. In this sense the intercalated materials such as pyridine- $\text{TaS}_2$  are binary, while the intercalated bridge compound  $\text{Li}_x\text{Ti}_{1+y}\text{S}_2$  is a ternary system. Values of  $T_S$  above 20°K have been found<sup>9</sup> in the system  $\text{Nb}_3\text{Al}_{1-x}\text{Ge}_x$ , but again this system is pseudobinary, as both  $\text{Nb}_3\text{Al}$  and  $\text{Nb}_3\text{Ge}$  are stable and form continuous solid solutions with the same crystal structure. It may be correct to say that the high value of  $T_S$  in the  $\text{Li}_x\text{Ti}_{1+y}\text{S}_2$  intercalated bridge system is the first example to be found of a new class of ternary materials, and that the values of  $T_S$  attainable in true ternary structures may exceed those so far attained in binary structures by as much as  $T_S(\text{Li}_x\text{Ti}_{1+y}\text{S}_2)$  exceeds  $T_S(\text{NbS}_2)$ —i.e., about a factor of 2.

In summary, the microscopic model presented here supports the conclusion already emphasized by Barz *et al.*<sup>5</sup> that for purposes of superconduc-

tivity the compound  $\text{Li}_x\text{Ti}_{1+y}\text{S}_2$  should not be described as an intercalation compound. Rather it is primarily a bridge compound, with intercalation of Li atoms making possible a random distribution of bridge Ti atoms and hence a very large density of states at the Fermi energy. The Ti bridge atoms behave as a two-dimensional gas at 600°K, and are therefore “soft” at low temperatures, which is another factor contributing to the very high values of  $T_S$  observed.

I am grateful to Professor B. T. Matthias for several stimulating conversations.

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## Phonon-Assisted Tunneling through Amorphous Germanium

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We report the observation of electron tunneling between two metal electrodes separated by an amorphous germanium layer. Measurements of the derivative of the conductance with respect to the applied voltage yield the tunneling phonon density of states for amorphous germanium.

Electron tunneling has proved to be a valuable technique for studying the phonon density of states in solids.<sup>1</sup> For example, tunneling through II-VI-compound films has been used by Giaever and Zeller<sup>2</sup> to determine the longitudinal optical phonons of the compounds. They also reported observation of the LO phonon in a germanium barrier believed to be amorphous. In the present work, we have studied electron tunneling through amorphous germanium. We obtain from the data the tunneling phonon density of states of amorphous germanium. Its general structure is found to be reminiscent of the phonon density of states

of crystalline germanium as deduced from neutron-scattering experiments.<sup>3</sup>

The geometry of the samples, which allows four-probe conductance measurements, is shown in the inset of Fig. 1. The metal electrodes and the germanium layer are evaporated by Joule heating in an oil diffusion pumped vacuum system, equipped with a liquid-nitrogen cold trap and a water-cooled baffle. The pressure is always lower than  $10^{-6}$  Torr before evaporation, rising to  $2 \times 10^{-6}$  Torr at most during the germanium deposition. The substrate (microscope glass plate) is kept at low temperature during the aluminum