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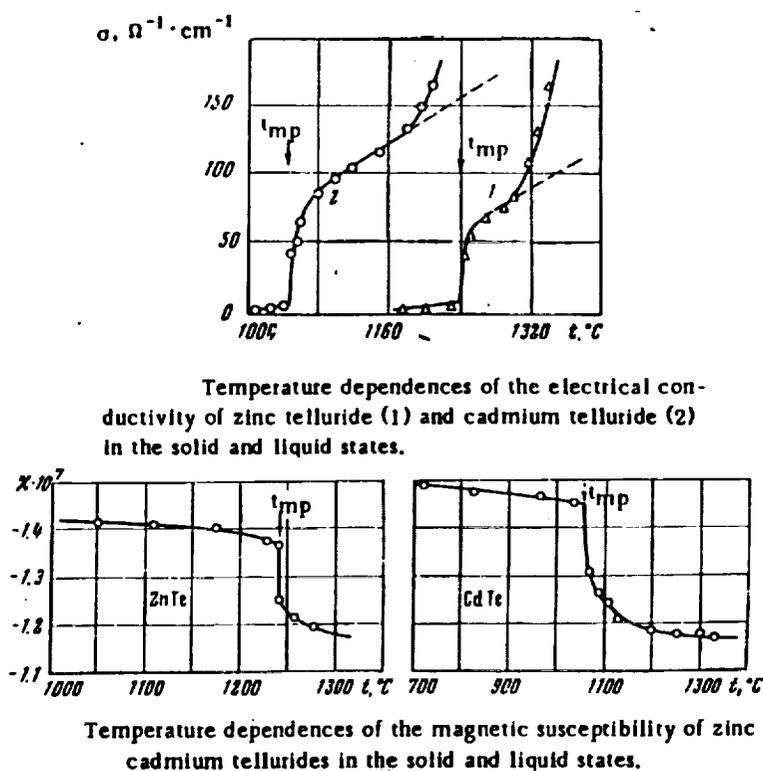


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16. Abstract  <p>We have carried out numerical calculations of the electronic properties of liquid II-VI semiconductors, particularly CdTe and ZnTe. We have been able to model the measured conductivity of these liquid alloys by assuming that the dominant temperature effect is the increase in the number of dangling bonds with increasing temperature. For low to moderate values of electron correlation, our calculated conductivity as a function of dangling bond concentration closely follows the measured conductivity as a function of temperature. We have found that both the temperature dependence of the chemical potential and the thermal smearing in region of the Fermi surface have a large effect on our calculated values of conductivity.</p>					
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## FINAL REPORT OF FNAS COMPUTATIONAL MODELING

We have investigated the electronic properties of liquid II-VI semiconductors, particularly CdTe and ZnTe. Only a very limited amount of information about these materials exists in the literature. The most extensive work was done by Glazov and co-workers<sup>1,2</sup> who measured the conductivity, viscosity, density, and magnetic susceptibility as a function of temperature up to temperatures well above the melting points. Their measurements show that these semiconductors retain their low coordination number and remain non-metallic even above their melting points unlike Si, Ge, and the III-V semiconductors. Figure 1 reproduces their conductivity<sup>3</sup> and magnetic susceptibility data.<sup>3</sup>



**Figure 1**

From the low conductivity found in the liquid state and the only reported neutron diffraction studies<sup>4</sup> of liquid CdTe, we can infer that CdTe and ZnTe retain their underlying covalent bond structure into the liquid state. However,

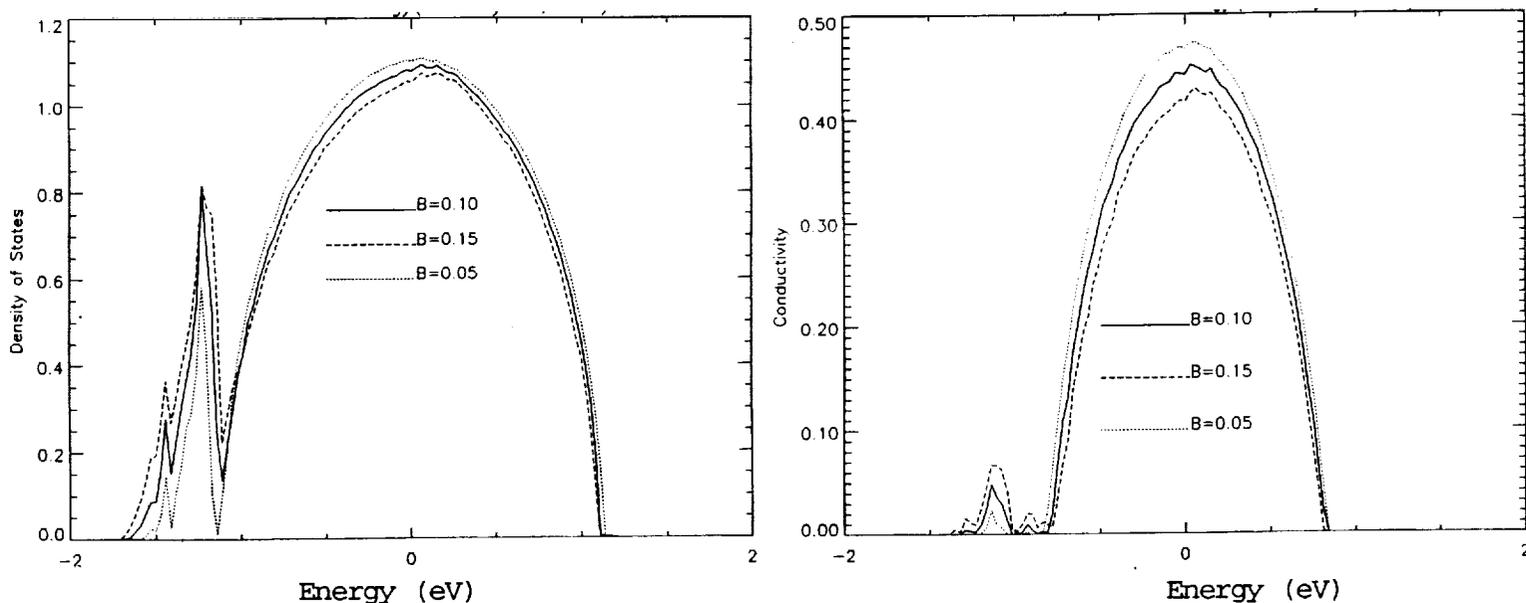
the rapid but continuous decrease in the diamagnetic susceptibility and the decrease in viscosity above the melting point both indicate that the number of broken bonds increases rapidly at the melting point and then continues to increase as the temperature rises. The broken bonds must create unpaired electrons (dangling bonds) that introduce a paramagnetic component to the susceptibility.

We have attempted to develop a model that would allow us to reproduce the conductivity measurements. Our model is based on the premise that the number of broken bonds increases with temperature above the melting point and that states associated with these dangling bonds lie in the energy gap of CdTe and ZnTe. The most notable feature of the measured conductivity curves is that just above the melting point the conductivity increases gradually with temperature for about 100 C and then increases much more rapidly up to the highest temperatures for which measurements were made. It appears that a metal-nonmetal transition will occur at about 200 C above the melting point. Such a transition could occur because of increasing overlap between localized dangling bond states or because of increasing overlap between the dangling bond states and the conduction band. The goal of our calculations has been to model such transitions.

We have carried out numerical calculations of the density of states and conductivity as a function of energy. The calculations have been performed using a Green's function technique developed previously<sup>5,6</sup>. We start with a tight-binding Hamiltonian which contains a diagonal on-site term and an off-diagonal nearest neighbor hopping term. We have assumed that the band gap remains large even in the liquid state and that the additional states introduced into the gap by the broken bonds lie near the conduction band edge. This has allowed us to focus on the interaction between the band created from the dangling bond states, hereafter referred to as the impurity band, and the conduction band and to ignore valence band interactions. The important parameters in our calculations are the energy separation between the conduction band and the impurity band and the concentration of the impurity band states. We have used a Monte Carlo technique to develop the local environment of each site. In most of our calculations we have assumed that the sites associated with the impurity states are distributed randomly. The

hopping term in the Hamiltonian introduces three additional parameters: the overlap integrals between the host atoms (no dangling bonds), between the host atoms and the impurity atoms (those with dangling bonds), and between the impurity atoms. In most of our calculations we have taken all three of these parameter to be equal.

Figure 2a shows the density of states as a function of energy for three different impurity concentrations (labeled B), corresponding to three different temperatures. The impurity band lies below (to the left of) the host band and contains 5%, 10%, and 15% of the states. The increasing overlap between the impurity band and the host band as the impurity concentration increases is evident. For the calculations shown in this figure, the energy separation between the host and impurity sites was taken to be 0.9 eV, but the center of the impurity band can be seen to lie 1.4 eV below the center of the host band, showing the repulsion between the bands. Figure 2b shows the conductivity as a function of energy for the same impurity concentrations as in figure 2a. For energies that lie within the impurity band, it can be seen that the conductivity is quite low even when the density of states is high. This is a clear indication that the mobility of the impurity band states is quite low.



**Figure 2**

**The density of states versus energy and the conductivity versus energy for three different impurity concentration.**

The measured properties of the material will depend critically on the position of the Fermi level (or chemical potential) within the bands. For instance, the measured value of the conductivity corresponds closely to the energy dependent conductivity in the neighborhood of the Fermi level. The position of the Fermi level in turn depends on the degree of electron corrections in the material. If we neglect electron correlations, each impurity state (dangling bond state) would contribute two states and one electron, causing the Fermi level to lie within the impurity band. If, on the other hand, we assume electron correlation to be large, then the impurity band would only containing states corresponding to single occupation of each impurity site and the states that correspond to double occupation of the impurities would lie at much higher energy, probably within the conduction band. In this case the Fermi level would be positioned so that the integrated area under the density of states curve up to the Fermi level would contain one state per impurity atom. For intermediate values of electron correlation, the Fermi level would lie in between these two extremes.

Figure 3a shows our calculated conductivity at the Fermi level as a function of impurity concentration for an intermediate value of correlation. We show this figure because it is one that reproduces the general shape of the measured conductivities in CdTe and ZnTe, showing a definite change in slope

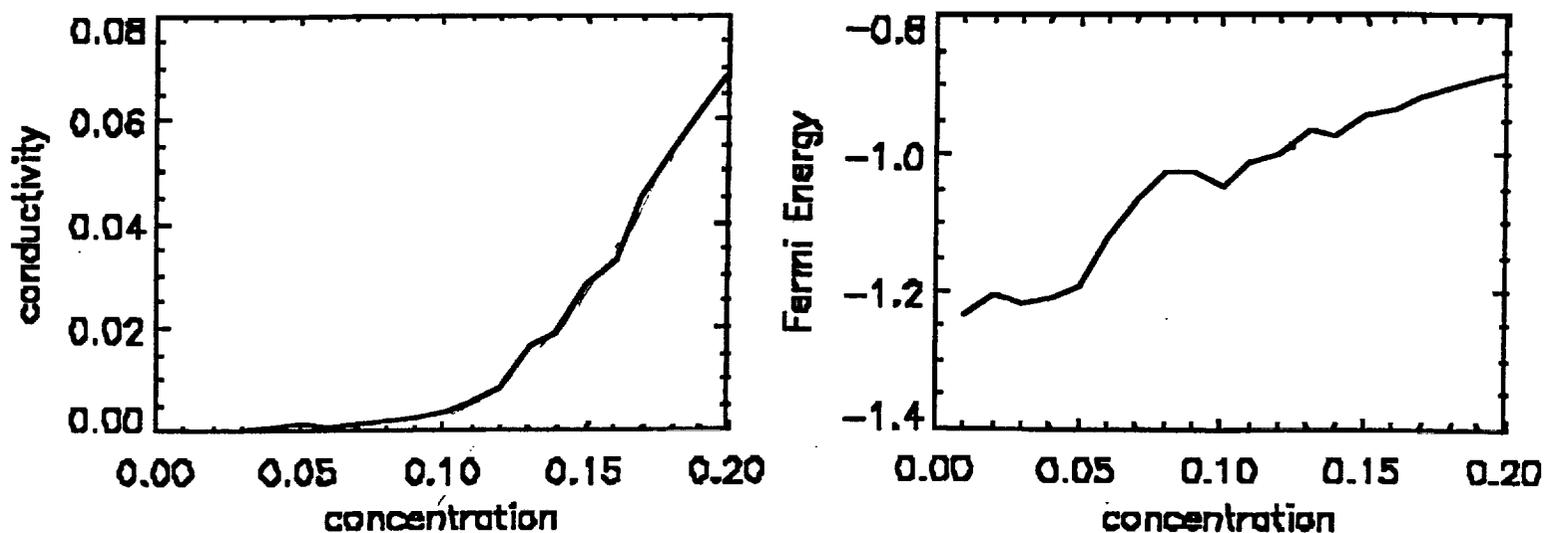
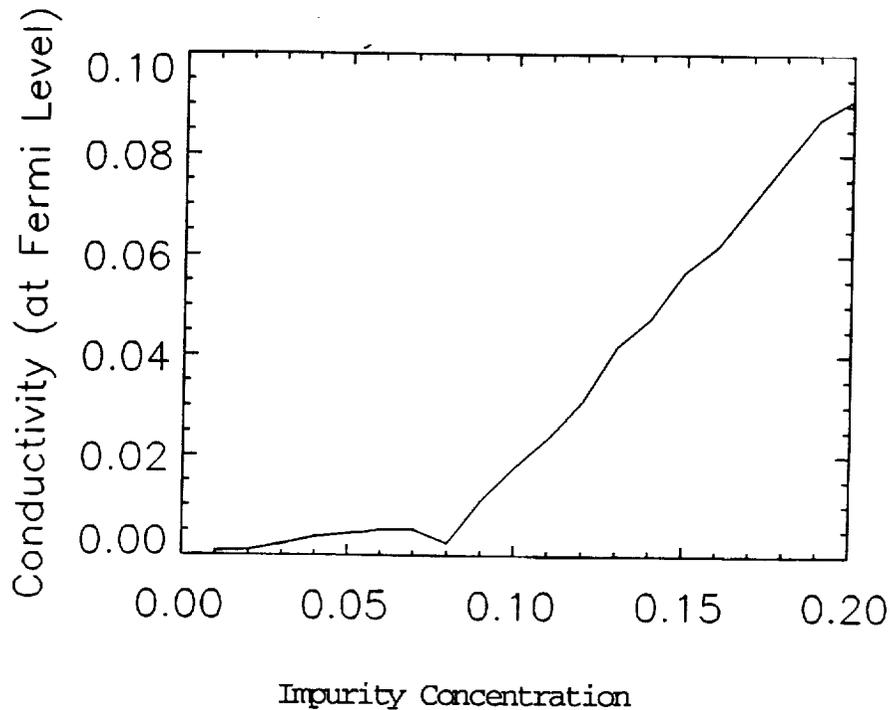


Figure 3

The conductivity at the Fermi energy as a function of impurity concentration and the Fermi energy as a function of impurity concentration

for an impurity concentration of about 12%. To get the absolute calculated conductivity from the relative conductivity shown on the graph, it is necessary to multiply by a scaling factor of  $1.1 \times 10^4$ . Thus the calculated conductivities are the correct order of magnitude. Figure 3b shows the position of the Fermi level as a function of impurity concentration and allows one to understand the behavior of the conductivity.

As the impurity concentration increases and the impurity and host bands overlap more, the Fermi level moves upward in energy. At a concentration of about 12%, it enters the host band (with band edge at  $\sim -1.0$  eV) and for higher concentration, the conductivity then increases rapidly. Figure 4 shows another graph of conductivity versus impurity concentration for intermediate correlation but somewhat different parameters in the Hamiltonian.



**Figure 4**

**The conductivity at the Fermi energy versus impurity concentration.**

We have found that we can only produce curves of this shape for low and intermediate values of electron correlation. For the case of large correlations, the Fermi level always lies in the host band and the conductivity increases monotonically with impurity concentration.

Because our calculations are meant to describe materials at relatively high temperatures ( $>1000$  K), we realized that the temperature dependence of the Fermi level (chemical potential) and thermal smearing at the Fermi level could be important. To take account of these effects, we first determined the correct temperature-dependent Fermi level using charge neutrality and a careful numerical integration of the full Fermi function. We then used this Fermi level and a careful numerical integration of the energy-dependent conductivity using again the full Fermi function. Figure 5 shows the conductivity versus impurity concentration for large electron correlation with and without the temperature effects described above. It can be seen that the result of these temperature-dependent effects are small for large electron correlation where the Fermi level always lies within the host band. Note that the two curves, one with a temperature-dependent Fermi level and the other without, lie almost on top of each other.

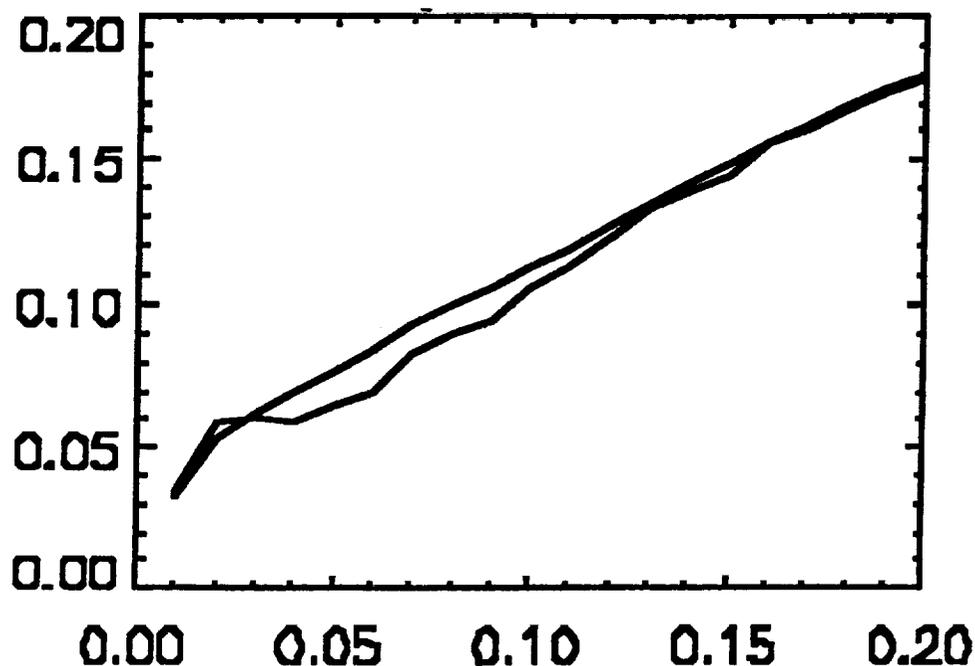
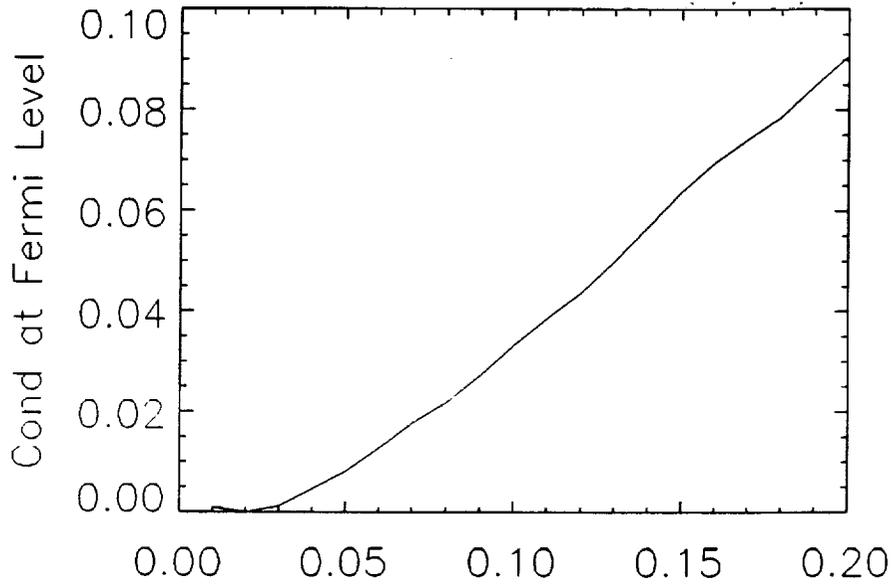


Figure 5

**The conductivity versus impurity concentration for large electron correlation with and without the effects of thermal smearing and the temperature dependent chemical potential.**

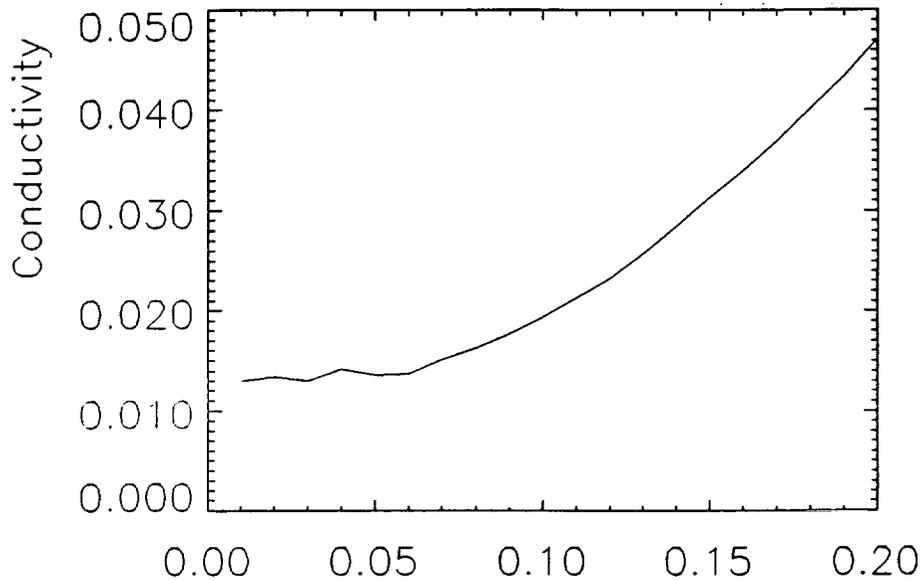
For small electron correlation, however, these temperature-dependent effects are large. Figures 6a and 6b show one set of our results for conductivity versus impurity concentration with zero electron correlation. Here one can see a marked change between the two curves: in 6a thermal smearing and the

temperature shift of the chemical potential were neglected while 6b includes them.



**Figure 6a**

**The conductivity at the Fermi energy as a function of impurity concentration.**



**Figure 6b**

**The conductivity at the chemical potential as a function of concentration.  
This curve includes the effects of thermal smearing.**

If we can assume that the impurity concentration range shown, 1% - 20%, corresponds to the number of broken bonds in CdTe in the range from just above the melting point to the limit of the experimental measurements (see

figure 1), then the agreement with experiment is excellent. We are still investigating the range of parameters that will produce this excellent agreement.

Although there has been very little theoretical work done on liquid semiconductors, we have continued to look for other systems that have been more thoroughly investigated. One area from which we have learned is that of amorphous semiconductors where there is an extensive literature.<sup>7</sup> The thermal smearing and temperature shifts of the chemical potential we referred to above are also important in amorphous semiconductors. The largest difference between liquid and amorphous semiconductors is that liquid semiconductors are in a thermodynamic equilibrium state and amorphous materials are not, so that the important dangling bond states that lie in the energy gap may be quite different in nature.

From our completed work, we have been able to show that we are able to model the measured conductivity of liquid CdTe and ZnTe alloys by assuming that the dominant temperature effect is an increase in the number of the dangling bonds with increasing temperature. As yet, we do not know how to calculate the number of these bonds as a function of temperature, so we have had to use the concentration of dangling bonds as a free parameter. We find that for the region of 10% to 20% dangling bonds we obtain the correct order of magnitude for the conductivity for certain ranges of the key parameters. We have also found that electron correlation has a large effect on the conductivity and that under certain conditions the temperature dependence of the Fermi level and thermal smearing can also produce large effects. We have submitted an abstract of our results for the March meeting of the American Physical Society and will report on our results at that meeting.

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