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Alvarez, Carmen Varea de
Cohen, Marvin L.
Ley, L.
et al.

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Carmen Varea de Alvarez, Marvin L. Cohen, L. Ley,
S. P. Kowalczyk, F. R. McFeely,
D. A. Shirley and R. W. Grant

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ELECTRONIC DENSITY OF STATES AND BONDING IN CHALCOPYRITE-TYPE SEMICONDUCTORS*

Carmen Varea de Alvarez† and Marvin L. Cohen†

Department of Physics and I.M.R.D.,
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

and

L. Ley, S. P. Kowalczyk, F. R. McFeely, and D. A. Shirley

Department of Chemistry and
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

and

R. W. Grant

Science Center,
Rockwell International
Thousand Oaks, California 91360

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Abstract:

Measured XPS spectra for $ZnGeP_2$ and $CdSnAs_2$ are presented along with density of states, N(E), and charge density calculations for $ZnGeP_2$. Analysis of the density of states spectra illustrates the relation between N(E) structure and bonding properties, allowing spectral peaks to be assigned to specific bonds.

We have calculated the valence-band density of states N(E) and measured the x-ray photoemission (XPS) spectrum I(E) for the chalcopyrite-type semiconductor $ZnGeP_2$. I(E) was also measured for $CdSnAs_2$. In $ZnGeP_2$ the shapes of N(E) and I(E) agreed very well, allowing us to correlate structure in I(E) explicitly with Zn-P and Ge-P bonds through contour plots of electron charge densities integrated over selected energy intervals, $\rho_{\Delta E}(\vec{r})$. This approach appears promising for a detailed understanding of bonding in chalcopyrite-type compounds and other ternary or more complex materials.

The $A^{II}B^{IV}C_2^{V}$ compounds are ternary analogues of the $B^{III}C^{V}$ zincblende semiconductors (e.g., $ZnGeP_2$ is the analogue of GaP) in which alternate cation sites are occupied by atoms of the Group II and Group IV elements surrounded in tetrahedral coordination by Group V anions. The ternary compounds therefore possess an essential complication that is absent in their binary analogues--two kinds of bonds. The present work represents the first attempt to relate features in N(E) or I(E) to different bonds in a relatively complex material, thereby extending a correlation that is obvious for the diamond and zincblende lattices.[1,2]

Our approach was to compute the charge density $\rho_{\Delta E}(\vec{r})$ within an energy region ΔE rather than the usual $\rho_n(\vec{r})$, the charge density for band n. The energy region was chosen to correspond to an energy interval in which N(E) contains structure of interest (e.g., a peak). For $ZnGeP_2$ there appears to be six important regions in N(E). These are labeled A, B, C, D, E, and F in Fig. 1. Figure 2 shows $\rho_{\Delta E}(\vec{r})$ for each region, calculated in the x = y plane, which contains the Zn, Ge, and P ions. The experimental results will be described next, followed by a discussion of the calculation and an analysis of the results.

Single crystals of $ZnGeP_2$ and $CdSnAs_2$ were grown by directional solidification of stoichiometric melts synthesized from the elements. The photoelectron spectra were measured in a Hewlett-Packard 5950 ESCA Spectrometer (which uses monochromatized AlK_α x-rays) modified to operate at pressures well below 10^{-9} Torr. Samples of the single cyrstals were fractured inside the spectrometer immediately before the measurements. The freshly exposed surfaces showed no detectable oxygen or carbon contamination even after 12 hrs. Valence-band spectra I(E) referred to the top of the valence band are shown in Fig. 1. These spectra have been corrected for contributions from inelastically scattered electrons.[3] The intense peaks corresponding to emission of core-like Zn 3d and Cd 4d electrons have been truncated to exhibit the valence s and p contributions more clearly. The unperturbed shape of the d peaks is indicated by solid curves in Fig. 1.

We first give a brief description of the spectrum which we will analyze in detail later. Starting at the top of the valence band, I(E) rises in both compounds to an intense, broad peak at a binding energy of 2-4 eV. This peak exhibits a wealth of fine structure. After a well defined minimum at 6.2 eV in $ZnGeP_2$ and 5.7 eV in $CdSnAs_2$, the intensity rises again. In $CdSnAs_2$ a blunt hump is observed around 7.0 eV, with a satellite at 8.3 eV. Beyond 8.5 eV I(E) follows closely the sharp onset of the leading edge of the 4d peak. Valence-band contributions to I(E) cannot be distinguished at higher binding energies.

In $ZnGeP_2$ a second region of high valence-electron density can be identified around 7.0 eV on the leading edge of the Zn 3d peak. A drop in intensity of peak II beyond 8.0 eV seems likely, but is not certain. There is a shoulder on the low energy (high binding energy) side of the Zn 3d peak which cannot be explained by oxidation, plasmon losses, multiplet splitting or shakeup processes.

We therefore interpret that shoulder as due to a third valence band peak centered at ∿ 12.5 eV with a total width of about 4 eV at its base. This determines the total valence bandwidth in $ZnGeP_2$ as 14.5 ± 0.5 eV. A corresponding third peak in $CdSnAs_2$ is presumably masked by the Cd 4d peak. Its position is then limited to a range of between 10.0 eV and 12.5 eV.

The band structure calculations for $ZnGeP_2$ were based on the Empirical Pseudopotential Method.[4] No attempt was made to fit the pseudopotential to experiment. The method of choosing the potential and the resulting band structure is given in Ref. 5.

In analyzing the band structure, it is helpful to use the quasicubic model.[5] In this model, the band structure of the chalcopyrite semiconductor is viewed as a perturbed version of its zincblende analogue. In a typical zincblende semiconductor, N(E) exhibits the following prominent structure:[1] A broad peak (peak I) near the top of the valence band, separated from a second narrower peak (peak II) by a small valley, followed by a gap which separates this structure from the lowest energy peak III. Charge density calculations[2] for each of the valence bands separately give some indication of the electron distribution in the zincblende case. States in peak I correspond to electrons near the bonding sites, peak II contains electrons which are mostly s-like around the cation and some charge piled up in the bonding region, and peak III contains electrons which are s-like around the anion.

In the chalcopyrites one expects that the overall N(E) should be similar, but that more structure should be present. For example, peak I should contain structure arising from the two types of bonds. Since this calculation was based on a local pseudopotential one expects the same problems that were encountered with local pseudopotentials for the zincblendes.[2] In particular, a non-local scheme[2,6] was necessary to obtain the correct width of peak I in the zincblendes. The local potential gives a peak I which is too narrow. We therefore expect the peak I region to be too narrow in the chalcopyrite case; however the basic features of the structure should not be affected.

Figure 1 contains the results for the calculated N(E) for $ZnGeP_2$ and the measured XPS spectra for $ZnGeP_2$ and $CdSnAs_2$. Critical points in the band structure show up as sharp structure in N(E). To facilitate comparison with experiment a Gaussian broadened curve N'(E) is also shown. Figure 2 shows $\rho_{\Delta E}(\vec{r})$. The energy intervals ΔE were chosen through analysis of N'(E); $\rho_{\Delta E}(\vec{r})$ was then calculated for each interval by restricting the band indices and k-states to give electron states in the desired energy range ΔE.

Referring to Fig. 1 we see that the highest energy (lowest binding energy) valence-band structure, which corresponds to peak I in the zincblende case, is split into two regions, A and B. Using the $\rho_A(\vec{r})$ and $\rho_B(\vec{r})$ of Fig. 2, we see that these regions contain electrons in the Zn-P and Ge-P bonds, respectively. The number of electrons in the energy interval A is 11.4 and there are 5.45 electrons in the B region. Peak I is therefore split by the energy difference in the two bonds. The Ge-P bond appears to be a stronger covalent bond (i.e., it lies lower in energy) than the Zn-P bond, as would be expected on chemical grounds. The theoretical width of peak I is smaller than experiment; this could arise either from the use of the local potential as described before or from an underestimation of the difference between the potentials of the two cations.

The general shape and splitting of peak I, however, shows excellent agreement between the experimental and theoretical spectra, with four distinct corresponding features present in each.

The peak-II region splits into three peaks C, D, and E. In the binary semiconductors, $\rho(\vec{r})$ shows some concentration around the cation with some charge in the bond. For $ZnGeP_2$ in the C region (3.15 electrons) charge concentrates on Zn with some charge in the Ge-P bond while region D (2.05 electrons) and E(1.95 electrons) show charge accumulating on Ge. This order is expected because the Ge potential is deeper than that of Zn. In region D there is some charge in the Zn-P bond while E shows some charge piled up in the antibonding region. In the XPS spectra, peak II is partially hidden by the d-peaks. In $CdSnAs_2$, by measuring the relative areas under the experimental spectrum and comparing this with the theoretical curve of $ZnGeP_2$, we conclude that the structure in the region between 6.5 eV and 7.5 eV probably corresponds to the D and C unresolved doublet. The satellite at 8.3 eV is interpreted as arising from region E. It is unfortunate that the peak II region is not easier to discern, as this region is most affected by the differences in the cation potentials.

As discussed before, peak III is observed in the $ZnGeP_2$ XPS spectrum, but hidden in the $CdSnAs_2$ spectrum. In the theoretical N'(E) this region is labeled F. There are 8 electrons in this region and $\rho_F(\vec{r})$ shows that the electrons are mostly s-like around the anion, i.e. the P site. This is the same configuration found in zincblende-type semiconductors. It is expected, as the phosphorous 3s subshell is tightly enough bound to be nearly corelike.

The above analysis illustrates the advantages of dealing with both $\rho_{\Delta E}(\vec{r})$ and N(E). We have concentrated on $ZnGeP_2$ in this work, but the results should be general for the chalcopyrite-type compounds. The possibility of identifying certain features in I(E) with well-defined charge distributions and specific bonds should be especially useful in the analysis of complex or amorphous materials, which as yet defy a realistic theoretical treatment.

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FOOTNOTES AND REFERENCES

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FIGURE CAPTIONS

Fig. 1. a) XPS spectrum for $CdSnAs_2$, b) XPS spectrum for $ZnGeP_2$, c) Broadened theoretical density of states for $ZnGeP_2$, d) Calculated valence band density of states for $ZnGeP_2$.

Fig. 2. Calculated electronic charge density contour plots for $ZnGeP_2$ corresponding to density of states peaks A, B, C, D, E, and F. The plots are normalized to the number of electrons contained in each peak. This value is given for each plot.

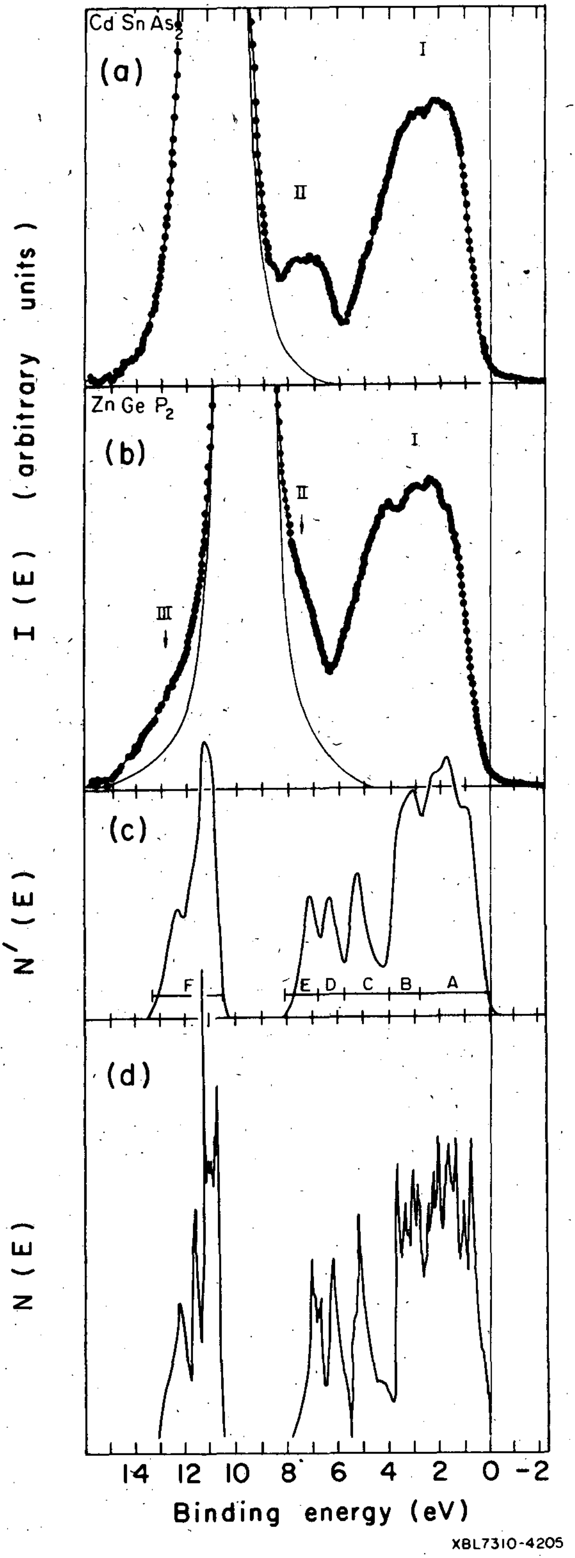
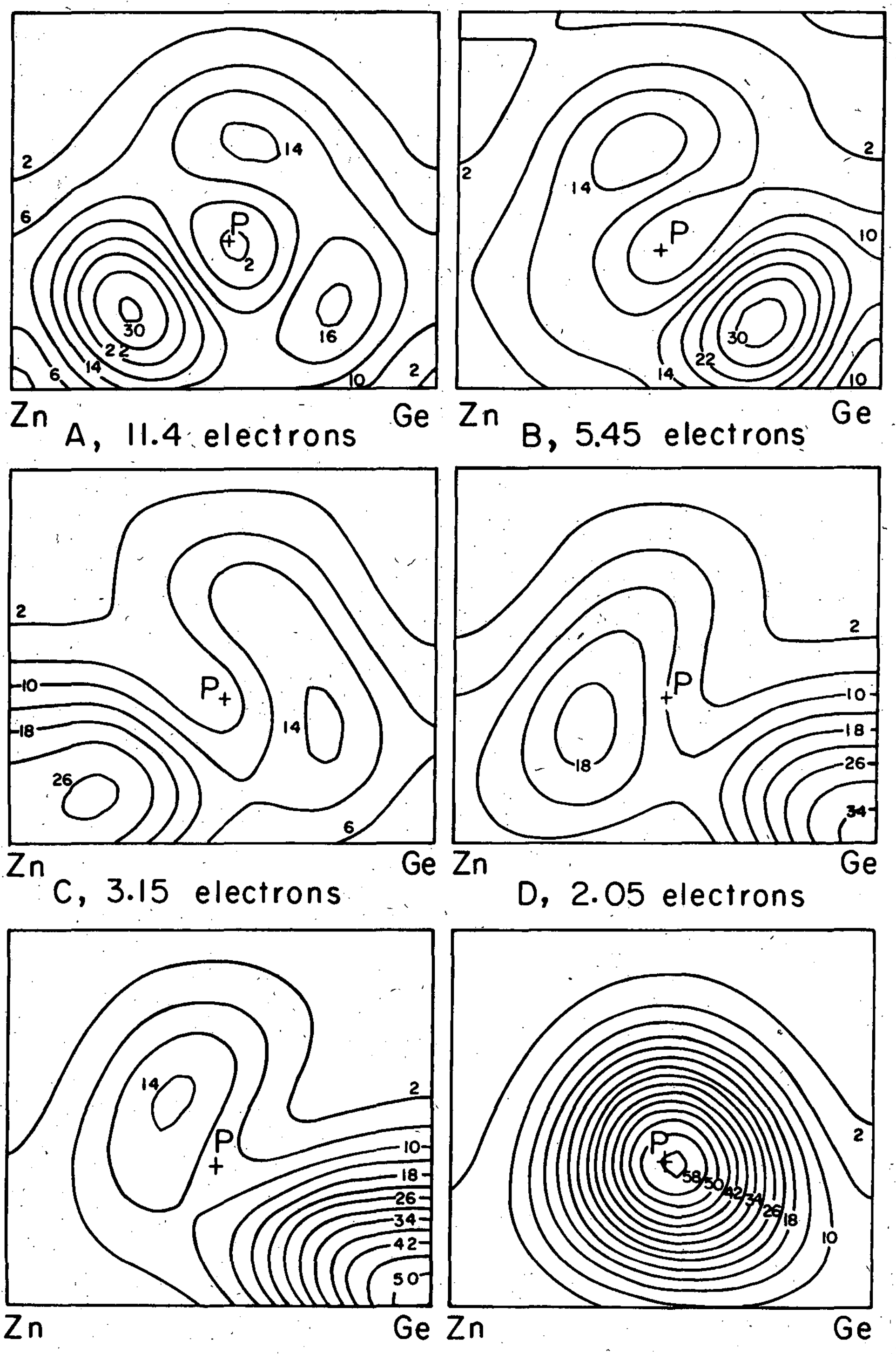

Cd Sn As2
(a)
I
II
Zn Ge P2
(b)
I
II
III
(c)
F
E
D
C
B
A
(d)
I (E) (arbitrary units)
N′(E)
N(E)
14
12
10
8
6
4
2
0
-2
Binding energy (eV)
XBL7310-4205

Fig. 1



A, 11.4 electrons
B, 5.45 electrons
C, 3.15 electrons
D, 2.05 electrons
E, 1.95 electrons
F, 8.0 electrons

XBL7310-4206

Fig. 2

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LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720