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Electronic Charge Densities in Semiconductors

Electron density calculations give new insights into the origins of the properties of solids.

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What holds a solid together? Where are the electrons in a solid? Why do elements and compounds exist in distinctive structures, and why do solids behave as insulators, semiconductors, semimetals, and metals? What is the origin of the optical and electronic properties of solids? Solid state theorists have posed questions of this type for many years, and in some cases they have supplied answers. Some of these answers have evolved from crude, suggestive explanations to precise, quantitative solutions that are now part of the literature of the field (*1*). Theorists have fared much better with electronic properties than with structural properties, and have concentrated on the former. Recently, however, there has been renewed interest in structural studies with emphasis on the bonding properties of semiconductors and insulators (*2, 3*).

It is likely that part of the reason why structural problems were not popular is that solid state theorists rarely work in real space. The successes in understanding the electronic properties of solids have been largely due to the band theory of electrons (*1*), from which we can obtain the energy states, $E(\mathbf{k})$, of an electron in a solid as a function of the electron wave vector $\mathbf{k}$. The $E(\mathbf{k})$ curves can be used to give information about the responses of solids to electric and magnetic fields (and other probes) in the low-frequency, optical, or high-frequency regions. In fact, this approach has been so useful that a majority of solid state theorists have been educated in wave vector (that is, momentum or "reciprocal") space. Because of this, they often give up the luxury of having a pictorial representation of the electron states of interests. Recently, however, energy band calculations have become so refined that wave functions for the electrons which are obtained in these calculations are accurate enough to give reliable probability densities for the electrons in solids (*4*). The main reasons for the refinements are the improvements in large computers and the use of experimental data by theorists to improve their calculations (*5*). The latter reason is the more important as it is possible to use optical data to fix atomic potentials very accurately. These potentials are then used to compute $E(\mathbf{k})$ and electronic wave functions.

The resulting electronic charge densities in solids—as in the case of molecules (*6*)—provide real-space models which, it is hoped, will lead to new concepts. They also make possible calculations (such as bonding calculations) which cannot be carried out easily by other methods.

In the following sections I will briefly describe some of the theory, display electron density plots that illustrate the properties of covalent and ionic bonds, and discuss the relation between bonding and crystal structure for a few simple structures. I will also discuss the questions I posed at the beginning.

Energy Bands, Pseudopotentials, and Charge Densities

To obtain charge densities and wave functions, the energy band structure, $E(\mathbf{k})$, must be calculated. This can be done by several methods, and the one we have used is the pseudopotential method (*5*). Pseudopotential theory is based on the division of electronic states into core states, which have the characteristics of atomic energy states, and valence states, in which the electrons are itinerant. For example, in the case of sodium, the electrons in the $1s$, $2s$, and $2p$ states would be core electrons, which are assumed to be nondeformable and to be identical whether the sodium atoms form a gas or a solid. However, the $3s$ valence electrons in the solid are free to wander through the crystal practically unhindered, giving sodium its high conductivity and metallic character. For silicon the core is the same as for sodium, but the two $3s$ and two $3p$ valence electrons are concentrated to some extent in the bonds between the silicon atoms.

This model of a solid illustrates a basic problem in band structure calculations. Near the cores the potentials are strong and rapidly varying. The electronic energy states are like those in an atom. Between the cores the potential is relatively weak and slowly varying, and the wave functions resemble those for free electrons or plane waves. Consequently, one does not have a good basis set to expand the wave functions. Atomic states are

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only good for core electrons, which are not of primary interest since the solid state effects are associated with the valence electrons. On the other hand, plane waves appear at first to be too unconfined to represent true valence states in a solid, particularly near the core.

There have been several successful methods for dealing with this problem. Pseudopotential theory is an outgrowth of one of them, the orthogonalized plane wave or OPW method (*7*). The central idea of the OPW method is to take a basis wave function in the form of a plane wave which is constructed in such a way that it is orthogonal to the core states. Because the OPW wave function is orthogonal to all the low-energy core states, it behaves near the core as if it were the next highest atomic state. Outside the core, it looks like a plane wave. This is precisely what we want. This is where the pseudopotential comes in. It is straightforward to convert into a potential the part of the OPW wave function that causes the orthogonalization to the core (*5*). The potential is repulsive since the orthogonalization terms have the effect of helping to keep the electrons out of the core. This repulsive potential cancels a large part of the strong, attractive core potential, leaving a net weak pseudopotential.

This is the essence of pseudopotential theory. It is possible to justify the existence of a weak potential that can be used to obtain the energy levels of the valence states in the solid. The wave functions obtained with the pseudopotential are equivalent to the real wave functions outside the core, but near the core they do not have the strong oscillations that the true wave functions have. However, the strength of the method lies in the fact that the energy eigenvalues are not pseudoenergies, but are identical to the eigenvalues obtained by using the true wave functions. Thus, the wave functions calculated from the pseudopotential represent the electrons very well, except near the cores.

The next question is how to get the pseudopotential for a crystal. The crystal pseudopotential can be constructed from the pseudopotentials for the atoms plus a structure factor that places the potentials in their appropriate positions in the crystal. The structure factor can be obtained from an x-ray analysis of the crystal. It is also convenient to deal with the Fourier transform of the pseudopotential, that is, the pseudopotential in reciprocal space. Because of the periodic symmetry of the solid, it is only necessary to know the atomic pseudopotential at specific wave vectors, which are the reciprocal lattice vectors, $\mathbf{G}$. Since the pseudopotential is weak and we are not interested in its magnitude near the core, the Fourier series can be cut off at relatively small wave vectors. For example, only the first three coefficients or form factors, $V(\mathbf{G})$, are necessary to obtain the energy levels for crystals like germanium or silicon in the diamond structure, so that the problem reduces to finding the $V(\mathbf{G})$'s for the atoms. The $V(\mathbf{G})$'s can either be calculated from atomic wave functions or obtained from experiment (*5*). The latter method is more accurate and is sometimes called the empirical pseudopotential method (EPM) (*5, 8*). I will briefly describe the EPM with emphasis on its use for semiconductors and insulators, although it can also be used for metals. In the example the $V(\mathbf{G})$'s are obtained from optical data.

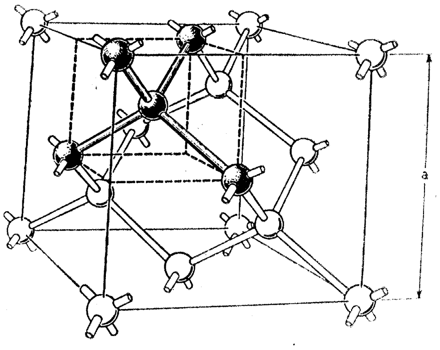


Fig. 1. The diamond crystal structure (*18*).

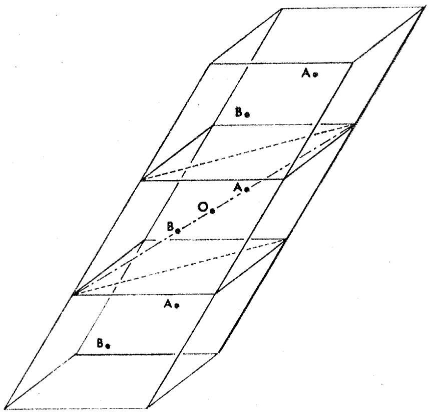


Fig. 2. Three primitive cells [smallest unit cell for the face-centered cubic structure (*1*)] showing the positions of the atoms (A and B). The intersection of the (1$\bar{1}$0) plane with the center cell is shown by the dashed lines. The (1$\bar{1}$0) plane bounded by its intersection with the primitive cell will be used to display the charge density.

The $V(\mathbf{G})$'s, obtained either from atomic wave functions or by fitting optical data for atoms, are considered to be approximate. These approximate form factors are then used in Schrödinger's equation, which is solved for the band structure, $E(\mathbf{k})$. Once the band structure is obtained it can be used to compute the frequency-dependent optical reflectivity, $R(\omega)$. The $R(\omega)$ curve usually has structure corresponding to the electronic energy gaps in $E(\mathbf{k})$. The calculated $R(\omega)$ can now be compared with a measured $R(\omega)$. It generally happens that the prominent optical structure is similar in both curves, but the theoretical curve is shifted from the experimental one, that is, the energy gaps in $E(\mathbf{k})$ are not quite correct. From an analysis of $E(\mathbf{k})$ and $R(\omega)$ it is possible to find the gaps that are responsible for the structure and their dependence on the $V(\mathbf{G})$'s. The $V(\mathbf{G})$'s are then changed until agreement is reached, at which point one has the correct pseudopotential, and an analysis of the optical data as a by-product. Often other experimental data besides the optical data are used, but optical data are the most convenient.

Once the $V(\mathbf{G})$'s have been determined and $E(\mathbf{k})$ obtained, the wave functions can be determined and used to compute the electronic charge density. The details and results of the latter calculation are described below.

Let me begin with the elemental semiconductors in group IV of the periodic table, which have the diamond structure (Fig. 1). The primitive cell for Ge contains two atoms, and each Ge atom has four valence electrons, so that there are eight valence electrons in a cell. If we examine $E(\mathbf{k})$ for Ge, the energy levels will be divided into bands. Each band represents the states for two electrons (spin up and spin down) in a cell. The diamond structure contains two atoms per unit cell, and there is an energy gap between the fourth and fifth bands. The eight valence electrons occupy the four bands below the gap, and these bands are therefore called valence bands. It is the energy gap that gives rise to the extremely useful properties of semiconductors (for example, in the transistor).

If we remain in the Ge row of the periodic table, we can construct compounds with eight valence electrons that are similar to Ge. Gallium arsenide is such a compound. It has a crystal structure similar to the diamond structure of Ge (Fig. 1), if the two Ge atoms in the unit cell are replaced by one Ga and one As atom. The latter structure is the zinc blende structure. Again there are eight valence electrons, three from Ga and five from As. There are many III–V semiconductors of this type, composed of elements from groups III and V in the same row of the periodic table. Another such compound in the Ge row is zinc selenide. This II–VI material also has eight valence electrons (two from Zn and six from Se) and exists in the zinc blende structure.

Let us return to the electronic charge density. Not only is it possible to calculate the charge density for the sum of the eight valence electrons—that is, the four valence bands—but the charge density ρ_n can be calculated for each individual band (labeled by the index n). The solution of Schrödinger's equation with the pseudopotential gives $E_n(\mathbf{k})$ and $\psi_{n,\mathbf{k}}(\mathbf{r})$ for each band, where $\psi_{n,\mathbf{k}}(\mathbf{r})$ is the wave function for a $\mathbf{k}$ state in band n. To obtain the charge density for band n we need to solve

$$\rho_n(\mathbf{r}) = e \sum_{\mathbf{k}} | \psi_{n,\mathbf{k}}(\mathbf{r}) |^2 \qquad (1)$$

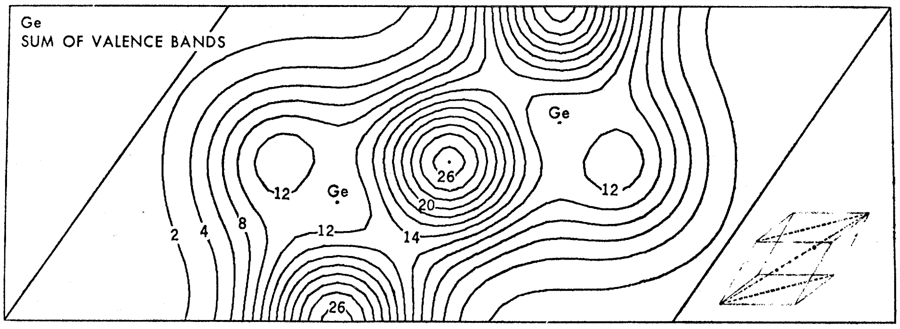
where the summation is over all available $\mathbf{k}$ states in band n, and e is the electronic charge.

Electron Charge Density Results

Since $\rho(\mathbf{r})$ is a three-dimensional function, it is convenient to choose a plane to illustrate the results. A suitable plane that contains the two atoms in the primitive cell (*1*) is a $(1\bar{1}0)$ plane, shown in Fig. 2. Values of constant $\rho(\mathbf{r})$ in this plane form contour plots (or relief maps). The units for $\rho(\mathbf{r})$ are e/Ω, where Ω is the volume of the primitive cell ($\Omega = \frac{1}{4}a^3$, where a is the lattice constant).

In Fig. 3 the calculated charge density for the sum of the four valence bands for Ge is given; this is the total charge density for all the valence electrons in Ge. The covalent nature of the Ge bond is demonstrated as the charge is piled up halfway between the two Ge atoms. The contours representing the bonding charge are well localized and egg-shaped, with a radius of about one-fourth the Ge-Ge distance (which is 2.45 angstroms). The contours for the core electrons are not shown here. They would give a very high concentration of electrons near the Ge sites. The radius of each Ge core is about one-fifth the Ge-Ge distance. The core radii were estimated by calculating the radius of a sphere containing 80 percent of the outermost shell of the Ge core electrons (by using atomic wave functions).

To demonstrate the nearly free-electron character of the conduction band states, the hypothetical charge density for the fifth Ge band is plotted in Fig. 4 as if it were filled. A constant charge density would result if the electrons were completely free. The small number of contours in Fig. 4 shows that the charge density distribution is nearly



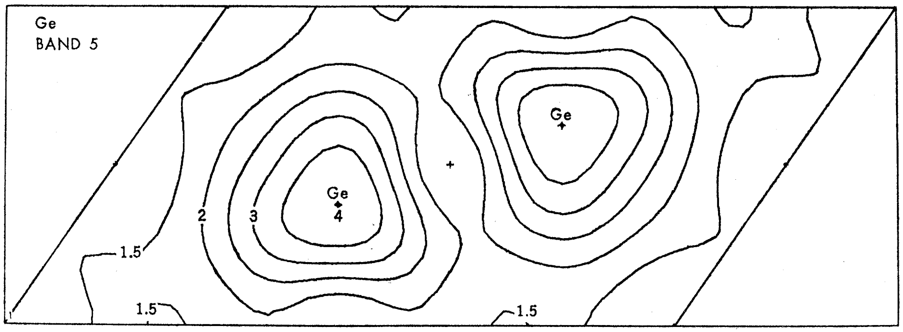
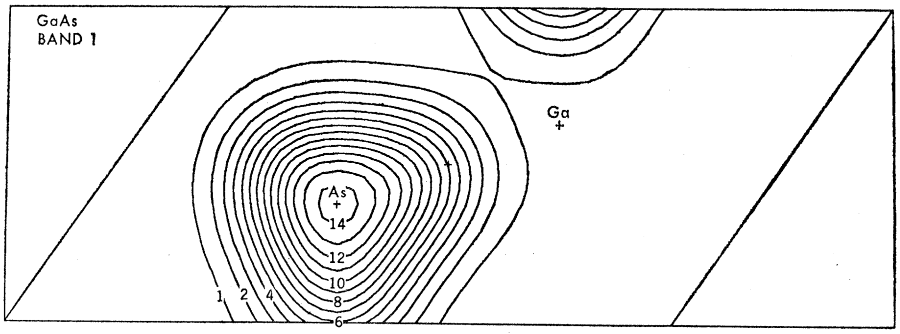


Fig. 3 (top). Total valence electron charge density (in units of electronic charge, e, per primitive cell) for Ge in the $(1\bar{1}0)$ plane. The radius of the Ge cores (not shown) is 0.20 of the Ge-Ge distance. This is the radius of a sphere containing 80 percent of the outermost shell of core electrons. Fig. 4 (bottom). Hypothetical charge density for the first conduction band of Ge.



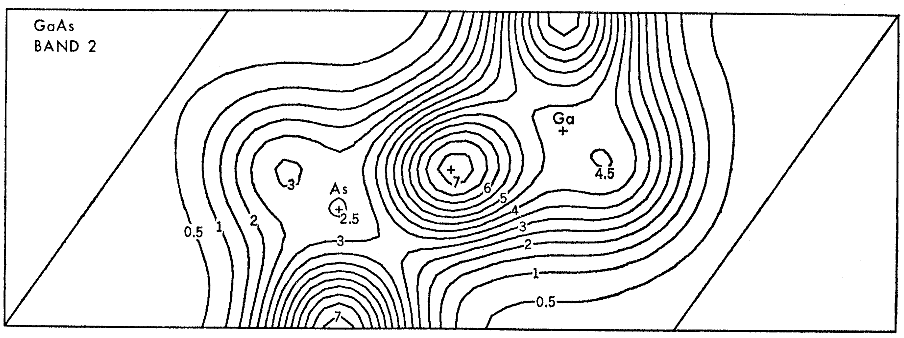
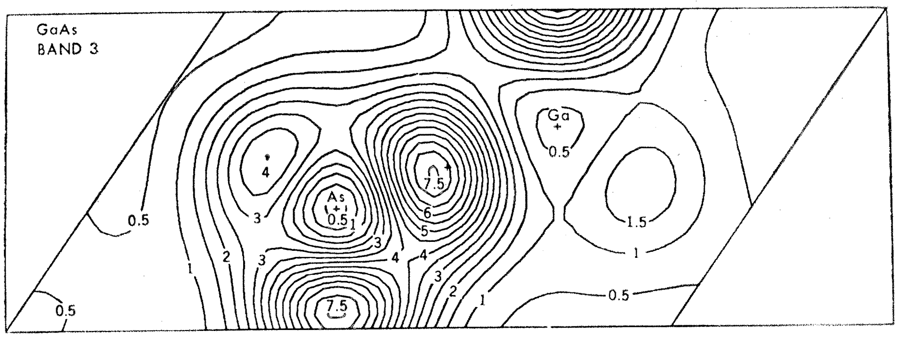


Fig. 5 (top). Valence electron charge density for band 1 of GaAs. The core radii for Ga and As are 0.23 and 0.18 of the Ga-As distance. The radii are those of spheres containing 80 percent of the outermost shell of core electrons. Fig. 6 (bottom). Valence electron charge density for band 2 of GaAs.

constant, with a slight concentration of charge at the atomic sites; there is no concentration of charge in the bonding region. Hence, the states in the first conduction band resemble those for free electrons, with some slight antibonding character. The valence electrons thus supply the bonding charge and form the covalent bond, while electrons that are excited to the conduction band are nearly free and capable of carrying electrical and heat currents through the crystal.

For GaAs, the valence electrons form a bond that is partially covalent and partially ionic. It is interesting to explore the contribution to the bonding from the electrons in each band. The effects are more easily understood if one considers building an imaginary crystal by using the eight valence electrons and the Ga^{3+} and As^{5+} ions or cores. Starting with the cores in their lattice positions, we can now add the valence electrons two at a time, by filling the valence bands one at a time. The results are shown in Figs. 5 to 9. In Fig. 5 the As^{5+} core attracts the first two valence electrons, leaving the less attractive Ga^{3+} ion almost bare. The distribution is like that in an atomic *s* shell around the As core, and the electrons cause the As ion to appear to be approximately an As^{3+} core. In band 2 (Fig. 6), the electrons distribute themselves in a more covalent arrangement with a mixture of *s* and *p* character, since the cores are now approximately equally attractive. For bands 3 and 4 (Figs. 7 and 8) the covalent charge is clearly displayed, but there is some shift toward the As ion. These states are *p*-like, and the charge is mostly concentrated between the cores. In the total charge density (Fig. 9), the charge densities of the individual bands add up to form a bond that is partially covalent and partially ionic. The covalent bonding charge is displaced toward the As atom.



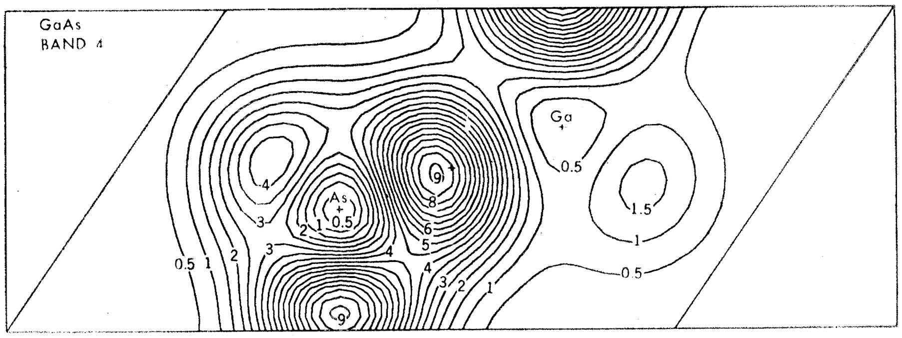


Fig. 7 (top). Valence electron charge density for band 3 of GaAs. Fig. 8 (bottom). Valence electron charge density for band 4 of GaAs.

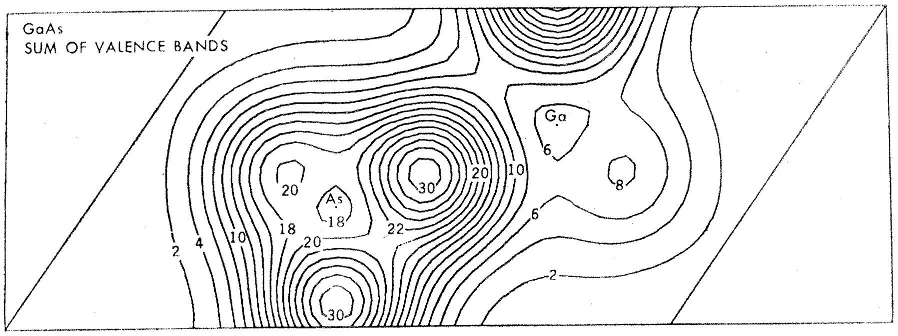


Fig. 9. Total valence electron charge density of GaAs: sum of valence bands 1 to 4.

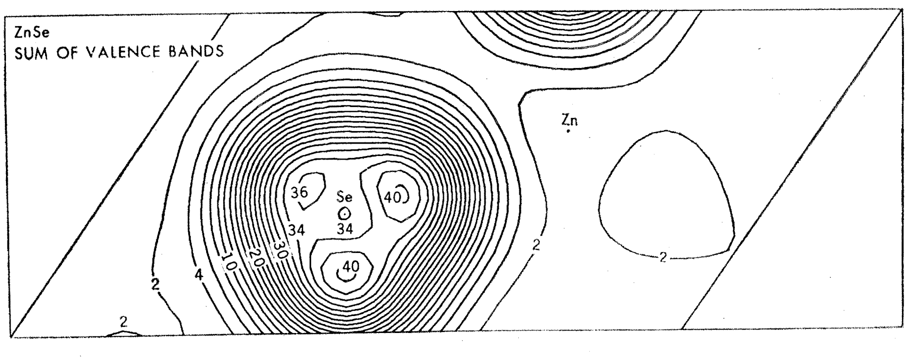


Fig. 10. Total valence electron charge density of ZnSe: sum of valence bands 1 to 4. The core radii for Zn and Se are 0.24 and 0.15 of the Zn-Se distance. The radii are those of spheres containing 80 percent of the outermost shell of core electrons.

In ZnSe the Zn and Se ions have charges of +2 and +6, respectively. Hence, the trend toward ionic bonding that is shown above on passing from Ge to GaAs is even stronger in ZnSe. Much of the charge becomes concentrated around the Se ion, but some covalent charge does remain in the bond. This is shown for the total charge density in Fig. 10. The covalent bonding charge is close to the Se ion, and it is shown by the rise in charge density above the large background in this region.

The materials Ge, GaAs, and ZnSe form an interesting series for studying bonding. The lattice constants and the wave functions for the core electrons are approximately the same for the three, and it is the valence electrons that give rise to the bonding properties. The series gray tin, indium antimonide, and cadmium telluride is similar in this sense, and calculations (*4*) for this group of semiconductors give results similar to those for the materials in the Ge row.

The tendency toward a more ionic bond in going from Ge to GaAs to ZnSe is clearly displayed in the charge density plots. Ionic bonding is characterized by a piling up of charge around the anion and a reduction of covalent bonding charge between the ions. It is the covalent bonding charge that is believed to be responsible for the stabilization of the tetrahedral structure for these compounds. Once the charge transfer is complete and the system can be thought of as a collection of charged ions (similar to NaCl), the fourfold coordinated structure is not stable with respect to the sixfold coordinated rock salt or NaCl structure.

To explore the role of the covalent bond it is useful to obtain a measure of the magnitude of the electronic charge in the bond. This is not easy, since the charge density background is varying and the bonding charge, Z_{b}, is not clearly defined. With the above statement serving as a caveat, we can calculate Z_{b} by integrating the charge density over a suitable region

$$Z_{\mathrm{b}} = \sum_{n} \int [\rho_n(\mathbf{r}) - \rho_0] d^3r \qquad (2)$$

where ρ_0 is the charge density at the outermost closed contour of the bonding charge density for each valence band. The integration is then done numerically over the volume described by the outermost contour. The values for Z_{b} (in units of e) are 0.146 for Ge, 0.080 for GaAs, and 0.026 for ZnSe. A similar calculation for the gray Sn row yields 0.123 for Sn, 0.091 for InSb, and 0.027 for CdTe. These values should be considered to be approximate for the reasons discussed above.

Since the bonding charge, Z_{b}, is expected to be related to the covalency of these crystals, we have compared this quantity with estimates of the ionicity or covalency by using the ionicity scales of Phillips and Van Vechten (*2*, *3*) and of Pauling (*9*). Following the notation of Phillips (*2*) the ionicity f_{i} can vary between 0 and 1. The value $f_{\mathrm{i}} = 0$ corresponds to a completely covalent crystal (such as C, Si, Ge, or gray Sn) while the value $f_{\mathrm{i}} = 1$ implies a completely ionic crystal with no covalent bonding. The Phillips–Van Vechten scale is based on estimates of the average energy gaps in semiconductors and insulators with eight valence electrons (the systems we are considering). The Pauling scale is used over a larger domain; we use here the values of ionicity for the Pauling scale that were given by Phillips (*2*).

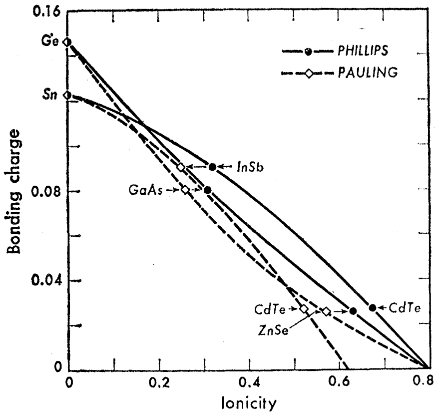


Fig. 11. Bonding charge versus ionicity. The bonding charge is in units of e per bond (see text).

It is interesting to note that an analysis of 68 binary crystals with eight valence electrons reveals that a critical ionicity value $f_{\mathrm{c}} = 0.785 \pm 0.01$ (Phillips–Van Vechten scale) separates the more covalent fourfold coordinated crystals (diamond, zinc blende, and wurtzite structures) from the more ionic sixfold coordinated crystals (rock salt structure). Although the determination of f_{c} is empirical, it is not too difficult to qualitatively understand the origin of the dependence of structure on f_{i}. It is expected that for $f_{\mathrm{i}} = 0$ the covalent bonding charge stabilizes the tetrahedral structure, or in terms of orbitals, sp^3 hybridization results in the tetrahedrally directed covalent bonds. When f_{i} becomes large, Z_{b} becomes small and tetrahedral coordination is lost. In fact, the bonding becomes electrostatic and sixfold coordination is preferred. One expects qualitatively that a transition from one structure to another should take place when Z_{b} is close to zero. (The real issue is the relative free energy for the structures, but this has not been calculated as yet.)

In Fig. 11, we plot our calculated Z_{b} against f_{i} for the Phillips–Van Vechten and Pauling f_{i} scales. Starting with the Phillips–Van Vechten scale, if the points for the series Ge, GaAs, and ZnSe are connected by a smooth curve and extrapolated to zero, the curve intersects the axis at $f_{\mathrm{i}} = 0.78$. A similar curve for Sn, InSb, and CdTe extrapolates to $f_{\mathrm{i}} = 0.79$. These are the values obtained as Z_{b} approaches zero. If we compare these with the empirical value for the structural change, $f_{\mathrm{i}} = f_{\mathrm{c}} = 0.785 \pm 0.01$, we find excellent agreement in these values. Considering the accuracy in the calculation and the fact that a structural change probably occurs before Z_{b} actually becomes zero, the excellent agreement between these values is somewhat fortuitous.

If the Pauling scale is used, the ionicity values for $Z_{\mathrm{b}} = 0$ are 0.80 for the Ge row and 0.61 for the Sn row. The critical ionicity [as determined by Phillips (*2*)] on the Pauling scale is 0.80. The value obtained for the Sn row is low, which seems to imply that for the crystals studied here the agreement with the Phillips–Van Vechten scale is somewhat better.

The relation of Z_{b} to f_{i} and the calculated ionicity value for the transition from fourfold to sixfold coordination are examples of the type of information one can obtain from charge density plots. Another interesting approach to studying the relation between electronic charge density and crystal structure is to compare the electron density computed for a compound crystallizing in one crystal structure with the electron density computed for the same compound in another structure (*10*, *11*). The object is to try to find differences in the electronic configuration that can be attributed to structural differences and to find some links between the electronic configuration and structure. The compound zinc sulfide is an ideal candidate for such a study since it exists in the zinc blende (cubic) and wurtzite (hexagonal) crystal structures. Both of these structures are fourfold coordinated, and the first and second nearest neighbors are located in the same positions in the two structures.

The structural differences do affect the electronic configuration. In the zinc blende case, the four nearest neighbors see the same environment. However, in wurtzite this is not the case, and because of this there is an asymmetrical distribution of charge about the sulfur atoms. This is best seen by examining $\rho(\mathbf{r})$ plots for cubic ZnS in the $(1\bar{1}0)$ plane (Fig. 12) and hexagonal ZnS in the (110) plane (Fig. 13). The units are in electron charge per primitive cell (two ions for zinc blende and four ions for wurtzite); the wurtzite structure was assumed to have an ideal ratio of the unit cell parameter c/a.

The electron density for cubic ZnS (Fig. 13) is very similar to that for ZnSe (Fig. 10), as expected, but in the hexagonal case the vertical bond shows a maximum ρ of about 76 whereas the diagonal bond has a maximum ρ of about 75. In addition to the asymmetry in the magnitude of the charge density between the diagonal and vertical bonds, the charge density in ZnS exhibits a "bulge"; that is, the maximum charge density is not along the

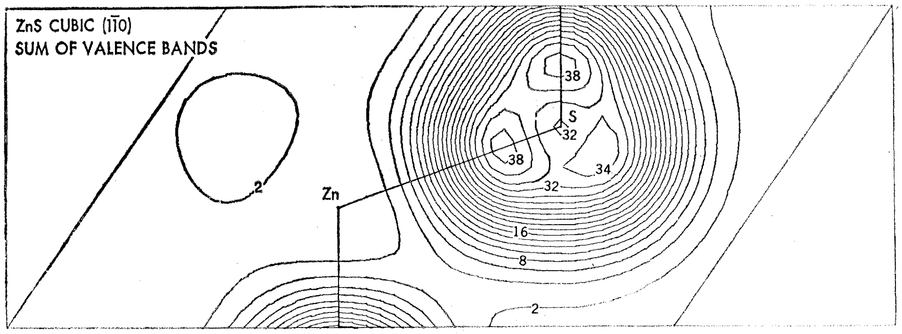


Fig. 12. Total valence electron charge density for cubic ZnS (zinc blende structure): sum of valence bands 1 to 4 in the $(1\bar{1}0)$ plane.

axis between the Zn and S ions. This bulge arises from the asymmetry in the assumed structure and could be predicted on the basis of classical electrostatics. The displacement in the charge suggests the possibility of electronic polarization in this wurtzite crystal with an ideal c/a ratio. Since the net polarization and the ideal c/a ratio are never found in real wurtzite crystals, it is tempting to speculate that the origin of the observed nonideal c/a ratios is the shifting of the atoms from the ideal positions to reduce the polarization of the ideal case. If this is the explanation of nonideal c/a ratios, it may be possible to calculate the observed c/a ratios by computing the c/a ratio necessary to obtain a theoretical zero polarization.

Summary, Recent Work, and Implications

In this section, I will discuss some of the questions posed at the beginning of this article, give some answers, and describe briefly recent results and work in progress that bear on the questions. Complete and detailed answers are not yet available for all these questions, but in some cases a great deal can be said to elucidate the physics.

The distribution of electrons in a solid can be described, at least to first order, by using the charge density plots. I expect that improved calculations with better pseudopotentials and wave functions will supersede the calculations displayed here, but I hope only in detail. Our calculations for solids, where we are dealing with 10^{23} particles per cubic centimeter, are at a more primitive stage than calculations for atoms or molecules (*6*), where refinements are expected only on a very fine scale. Better experimental techniques should yield more accurate numbers for the pseudopotential form factors. In fact, reflectivity measurements with wavelength modulation have been used to obtain a more refined InSb band structure (*12*). The charge density obtained in this calculation is very similar to that given here, and the bonding charge is only slightly smaller, making Fig. 11 a bit more linear. Changes of this order are expected to occur.

Another aspect of the charge distribution question which should be discussed is the domain of the calculations. I have described work on diamond, zinc blende, and wurtzite crystals. Calculations have also been made for PbTe (*13*) and NaCl (*14*) in the rock salt structure and for other zinc blende materials. Metals have also been studied, for example, aluminum (*15*), noble metals, and transition metal carbides such as NbC. Charge density plots for metals are much more constant than for semiconductors. For example $\rho(\mathbf{r})$ for Ge varies from about 1 to 27, with an average value of 8, while for Al it is between 1.7 and 3.4, with an average value of 3.

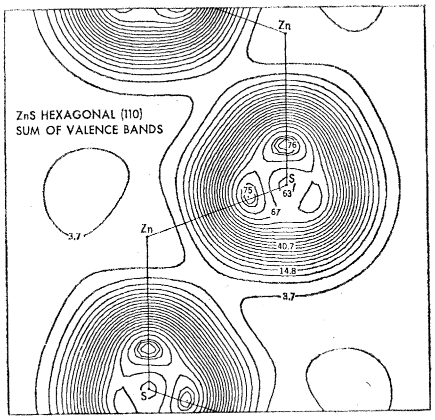


Fig. 13. Total valence electron charge density for hexagonal ZnS (wurtzite structure): sum of valence bands 1 to 8 in the (110) plane. Contour lines are shown with $\Delta\rho = 3.7$ up to $\rho = 62.9$. Contour lines for $\rho > 62.9$ are chosen without a fixed $\Delta\rho$ to illustrate the asymmetries in $\rho(\mathbf{r})$.

One can also ask about the consistency between theoretical electron distributions and experimental results. The first experiments that come to mind are those involving x-ray techniques. This problem is a difficult one. If a solid is described as a superposition of atoms, and atomic wave functions are used to explain the observed x-ray results, only small deviations are found. These small deviations test the correctness of the calculations. In cases where the x-ray data were considered to be accurate, comparisons reveal fairly good agreement between theory and experiment [for example, see the detailed study made for Al (*15*)]. New experimental techniques, such as x-ray Compton scattering, may provide more definitive tests for semiconductors. Comparisons of $\rho(\mathbf{r})$ obtained by the pseudopotential method with values obtained by other theoretical methods for computing wave functions, like the OPW method, yield reasonably consistent results.

The questions about optical and electronic properties have been answered to a large extent in terms of energy band structures and this area is a very mature one. I would expect that charge density calculations will not contribute in a direct way here, but they may be important conceptually. For example, the prominent features of the optical spectrum of Ge are understood in terms of electronic transitions between filled and empty states or bands. Once $E_n(\mathbf{k})$ is known, analysis of the reflectivity is made by associating peaks in the reflectivity with transitions between bands n and n' at a particular point in **k**-space in the Brillouin zone (*1*). This type of analysis is very powerful and usually completely satisfies a solid state theorist. However, it does not give a physical picture of where the electron is or where it is going in real space. If we choose the reflectivity of Ge as an example, electron density plots show that the first direct optical transition, at 1 electron volt, involves an initial state in which the electron is concentrated in the bond (between the atoms) and a final state in which the electron is on the atoms. The next peak in energy, at 2.2 electron volts (Λ peak), is similar except that the final state is a bit more spread out. The main peak in the Ge spectrum (the Σ-Δ peak at 4.3 electron volts) involves initial states concentrated in the bond and final states spread out in the cell and almost constant in density. These pictures of the states in real space may yield new insights into the physics of optical properties. It may be possible to use this approach to study the dependence of optical spectra on structure—or lack thereof, as in the case of amorphous semiconductors.

Theorists dealing with **k**-space can make good use of charge density plots and wave functions in real space for other calculations. Since wave functions associated with a specific point in **k**-space can be constructed, electronic properties (such as the pressure dependences of energy states) can be visualized in a manner similar to that used for optical spectra. Better methods of calculation may result because of this approach. For example, currently there has been interest in using Wannier wave functions as a basis set for electronic states in solids. These wave functions are localized real-space functions. It is fruitful as a test of the applicability of this scheme to construct the Wannier states, plot them in real space, and compare them with wave functions obtained from band calculations.

A recent advance will make studies of the type described above, involving charge density calculations, much easier and less expensive. In constructing the $\rho(\mathbf{r})$ function we used many points in **k**-space to compute $\psi_{\mathbf{k}}(\mathbf{r})$ for Eq. 1. It can be shown (*16*) that accurate $\rho(\mathbf{r})$ calculations (that is, of the order of 1 percent accuracy) can be made by using just a few **k**-space points. These points must be chosen in a prescribed manner, and the charge density associated with the points must be averaged in a specific way. This scheme reduces the labor and computer time involved in charge density calculations.

Coming back to the questions about the origin of the observed structures of solids and the bonding in solids, we have made some inroads by using electron distribution studies. Examples are the calculations involving the transition from fourfold to sixfold coordination, the pictures of covalent and ionic distributions of electrons, and the changes in electron density in going from the zinc blende to the wurtzite structure. These results are in some cases only qualitative; but the questions are difficult ones, since the energy differences between two possible structures are quite small on the scale of the energies computed in band calculations. Some recent work on structure and bonding involves an analysis of NaCl in the rock salt and hypothetical zinc blende structures (*14*), and calculations for materials in group IV (*17*). These studies give some insight into the question of why NaCl exists in the rock salt structure while GaAs prefers the zinc blende structure. Attempts have been made to explain the origin of covalent bonding and the strength of the covalent bond in going from carbon (diamond) to gray tin (*17*).

The case of diamond is particularly interesting. Because it has a simple $(1s)^2$ core, with no p state in the core, diamond is a difficult case for pseudopotential studies, where the orthogonality between valence and core states provides a repulsion of the valence states from the core. The $2p$ valence electrons must then be treated carefully, and it is these electrons that are prominent in determining the covalent bond. Preliminary studies have revealed some interesting effects (*11*). The bonding charge is found to be more spread out in diamond and, unlike Si and Ge, the minimum in the potential seems to be displaced from the halfway point between the atoms, so that there are two dips in the potential and possibly two humps in the charge density. (The preliminary calculations show the humps to be small, and the main feature is the spreading out of the charge.) If the carbon potentials are artificially forced closer together, so that the minima coincide, the interatomic distance becomes close to that of graphite. It is tempting to speculate that this peculiar nature of the carbon potential, compared with the Si and Ge potentials, is the reason why carbon forms multiple bonds and exists in many organic materials. My statements on carbon are speculative, but they illustrate the type of statements that may be useful in studies of crystal structure through charge density plots. I expect that much more work will be done in this area, and structural theories based on electronic charge density studies will result.

A by-product of the charge density calculations is the use of charge density plots as an educational tool. It is helpful to "see" the covalent bond and the changes that occur on passing from covalent to ionic bonding. I hope that these pictures will provide a useful conceptual background for future research on chemical binding and on the electronic structure of solids.

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