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Valence Charge Density in Indium Antimonide*

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Nine x-ray structure factors have been accurately measured in good-quality InSb single crystals and compared with various model calculations of the valence-electron charge distribution. Excellent agreement is obtained with a model based on tetrahedral distortion and ionic charge transfer, whereas Phillips's bond-charge model gave the poorest fit of all.

The nature of chemical bonding in tetrahedrally coordinated semiconductors is related to the spatial distribution of the valence-electron charge density. In $A_{\mathrm{III}}B_{\mathrm{V}}$ semiconductors the bonding is expected to be partly ionic and partly covalent, the latter component being responsible for departure from spherical symmetry.

Among the various models proposed for describing valence-electron charge densities, the most attractive for its simplicity is the so-called "bond-charge model," in which an interstitial accumulation of charge with spherical symmetry is supposed to exist along the bonds between nearest neighbors. Such a model, originally proposed by Ewald and Hönl[1] in 1936 in order to explain the nonzero intensity of the (222) x-ray reflection in diamond, and subsequently refined by Brill,[2] was recently redeveloped and extensively elaborated by Phillips who applied it to the III-V semiconductors and other crystals.[3,4] A number of properties such as ionicity, piezoelectricity, and lattice dynamics have been investigated using this model. Theoretical calculations of valence charge densities of various III-V crystals have also been recently performed using pseudopotential methods, and contour plots have been presented in the literature.[5] So far no direct experimental tests of these theoretical models have been available for III-V crystals. In the case of silicon, a comparison between experimental and calculated electron densities shows an overall fairly good agreement except for the shape of the bond maximum.[6]

It was found by one of us, a few years ago,[7] that x-ray reflections for which the two fcc lattices of the GaAs structure scatter out of phase (called in this paper "quasiforbidden") contain a good deal of information of about valence-electron asphericities. The reason for this is that the intensities of such weak reflections involve the difference between the Ga and As scattering form factors. Since the core charge densities are very similar for Ga and As, their scattering factors almost cancel out and a large fraction of the measured intensity is contributed by valence electrons. The core contribution can be accurately evaluated using Hartree-Fock (free-atom) wave functions. Any departure from spherical symmetry of the valence electrons is expected to produce appreciable effects on the measured intensities. These considerations are valid for all A_{III}-B_{V} crystals when A_{III} and B_{V} are in the same row of the periodic table.

This work reports a series of accurate x-ray measurements of quasiforbidden structure factors in InSb, with the specific purpose of comparing experimental results with different model calculations.

The integrated intensities of nine reflections with $h+k+l=4n+2$ $(n00, 1, 2, \ldots)$ have been measured in two large InSb single crystals of high quality,[8] cut parallel to the (100) and (111) planes.

The Bragg case of diffraction was used in a double-crystal arrangement, thereby minimizing thermal diffuse scattering contributions due to the fine collimation of the incident beam. The quality of crystal perfection was ascertained by measuring a few "strong" reflections ($h+k+l=4n$ or $2n+1$) whose intensities were found in good agreement with dynamical theory. Particular attention was paid to avoidance of multiple diffraction effects. The crystals were rotated around the diffraction vector and the measurements were taken at suitable azimuths so that no other reflection was excited at the same time. A perfect Ge crystal was used as a monochromator for the Cu $K\alpha$ radiation ($\lambda = 1.54$ Å), so that the polarization ratio of the incident beam could be calculated using dynamical theory. The intensity data were put on an absolute basis by measuring the incident beam with a series of calibrated absorbers. The accuracy of our measurements is estimated to be ±1%. The sum of the Debye-Waller factors for In and Sb was determined from the temperature dependence of the (800) and (444) reflections, whereas the difference was determined from the temperature dependence of the (600), for which bond-charge effects are very small. Anharmonic effects were evaluated using a simple theory developed for tetrahedrally coordinated crystals[9] and found negligible. Nine structure factors were measured at room temperature, with $\sin\theta/\lambda$ ranging between 0.15 and 0.51 Å^{-1}, and their values are presented in Table I. Several interesting features are immediately apparent from the values given in the table. The large discrepancies between experimental and free-atom values (spherical atom model) are due to asphericity of the valence electrons and charge transfer from In to Sb. The difference between (222) and ($\overline{222}$) is particularly noticeable because these two reflections should have exactly the same intensity, even considering the violation of Friedel's law as a result of anomalous dispersion. Such a difference is a direct consequence of a nonspherical charge distribution and tends to disappear with increasing values of $\sin\theta/\lambda$. The same structure factors listed in Table I can be calculated using different models for the charge density, and then compared with the experimental values. A convenient measure of the quality of a fit used by crystallographers is the reliability factor (or R factor) defined as

$$R = \sum |F_{\mathrm{exp}} - F_{\mathrm{calc}}| / \sum |F_{\mathrm{exp}}|,$$

where F_{exp} and F_{calc} are experimental and calculated structure factors. The pseudopotential values[10] exhibit the correct trends but tend to overestimate the effects due to the crystal potential. A slight improvement over the spherical-atom calculation is obtained in a least-squares fit with a Gaussian distribution along [111] between In and Sb and three adjustable parameters: the amount of bonding charge, the width of the Gaussian distribution, and the location of the maximum.

When the amount of bonding charge and the width of the Gaussian distribution are those of the bond-charge model proposed by Phillips,[11,12] the fit is the poorest of all. No improvement was

TABLE I. Experimental structure factors for InSb at 300°K. A comparison with different model calculations is made.

HKL	Experimental Value	Tetrahedral model	Gaussian model	Spherical Atom model	Pseudo-potential model	Bond charge model
200	7.20	7.25	7.17	6.77	7.86	5.21
222	7.79	7.73	8.11	6.54	9.63	8.58
$\bar{2}\bar{2}\bar{2}$	7.19	7.11	7.48	6.54	7.23	7.27
420	8.24	8.24	8.87	7.65	8.76	8.47
442	8.43	8.51	8.91	8.22	8.90	9.47
$\bar{4}\bar{2}\bar{2}$	8.57	8.57	8.91	8.22	8.88	8.93
600	8.44	8.53	8.90	8.22	8.83	7.65
622	8.28	8.29	8.58	8.08	8.57	8.22
$\bar{6}\bar{2}\bar{2}$	8.36	8.35	8.58	8.08	8.57	8.63
		R = .005	R = .042	R = .058	R = .065	R = .077

obtained when a Lorentzian form factor was assumed for the bonding charge. The model which provides the best fit is one based on a tetrahedral distortion of the outer electronic shells, and an ionic charge transfer from In to Sb. A similar model was proposed a few years ago for interpreting x-ray data in diamond, silicon, and germanium.[13,14] The basic idea is that the charge density of the valence electrons can be expanded in a series of cubic harmonics, in such a way that the overall symmetry of the nonspherical charge density is that of the atomic sites. We have extended this model to the Zn-Se structure by introducing an ionic charge transfer between two nearest neighbors, so that the charge density at any point in the crystal is expressed by means of spherically symmetric Hartree-Fock wave functions and two adjustable parameters. One of them, α, controls the amount of tetrahedral distortion, and the other one, λ, regulates an ionic charge transfer. Our analysis shows that this model provides an excellent fit with experiment, with an R factor more than an order of magnitude smaller than that obtained from the bond-charge model.

Measurements taken at various temperatures between 400 and 16°K indicate that the amount of charge transfer and tetrahedral distortion vary slightly with temperature. These results at different temperatures, along with a description of the experiments and model calculations presented above, will be reported with greater detail in a forthcoming article.

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Photoelectron Spin Polarization Testing the Ionic Structure of 3*d* Levels in Ferrites

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The dependence of photoelectron spin polarization on photon energy with ultrahigh-vacuum–cleaved surfaces of several ferrites shows that the electronic excitation spectrum of $3d$ states is described by the model of a single ion in a crystal field in all details. We obtain the relative intensity of the multiplet lines as well as the energy difference of $3d^{n-1}$ final states on A- and B-lattice sites with high precision.

At present, photoemission of electrons emerges as a handle on the old problem of whether the $3d$ states in a solid might be treated in analogy to the $4f$ shell by the model of a single ion in a crystal field (SICF). If this model applies, the structure in the energy distribution curves (EDC's) of photoelectrons emitted from $3d^n$ shells arises from the spectrum of the hole left behind and not from an initial band density of states. Support for this interpretation has been recently provided by photoemission spectra obtained with x-ray[1] and uv-photon energies. However, even in the