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Abstract

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EXPERIMENTAL DETERMINATION OF THE MAGNITUDE OF THE EFFECTIVE CHARGES OF IONS IN $A^{III}B^{V}$ COMPOUNDS FROM X-RAY DATA

One of the most important questions in the problem of chemical bonding in crystals, especially in semiconductor compounds, is the determination of the so-called degree of "ionicity" of the bond—the sign and magnitude of the effective charges of the ions forming the compounds. Of particular interest in this respect are the semiconductor compounds $A^{III}B^{V}$, which crystallize in the sphalerite structure.

According to existing views, the character of the chemical bond in compounds of the $A^{III}B^{V}$ type cannot be described as purely covalent, but belongs to a certain intermediate type between covalent and ionic. Pearson and Mozer (^{1}) proposed that the type of bond in semiconductor $A^{III}B^{V}$ compounds be regarded as a special type of "semiconductor bond." Slater and Koster (^{2}) considered a neutral type of bond, in which partial ionization of the atoms composing the compound is absent and, consequently, the ionic fraction is equal to zero. In works treating the chemical bond in $A^{III}B^{V}$ compounds as covalent, it is assumed at the same time that B^{V} atoms give electrons to A^{III} atoms. The A^{III} ions become negative, and the B^{V} ions positive. In the model proposed by Folberth (^{3}), on the contrary, it is assumed that A^{III} atoms acquire electrons, while B^{V} atoms give up electrons. As a result, the ionic charges become close to the following values: $A^{III\,3+}$ and $B^{V\,3-}$ atoms.

The available spectroscopic data indicate that in $A^{III}B^{V}$ compounds there is a certain "component of ionic bonding," i.e., that definite effective charges exist on the ions forming the compound. In the works of Spitzer and Fan ($^{4-7}$), estimates of the effective ionic charge for a number of $A^{III}B^{V}$ compounds were made from data of optical measurements of reflectivity in the infrared region and from absorption spectra. However, as Hillsum and Rose-Innes (^{8}) rightly note, these measurements give no information about the sign of the charges of the A^{III} and B^{V} atoms forming the compounds and, consequently, do not make it possible to decide which of these atoms gives up an electron and becomes a positively charged ion, and which accepts an electron and becomes a negatively charged ion.

In light of the foregoing, solving the question of the sign and magnitude of the

Fig. 1. Electron-density distribution map in the (110) plane of the elementary cell of aluminum antimonide. The ion boundaries of Al and Sb are indicated by a dashed line.

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charges acquires exceptionally great importance for forming correct ideas about the nature of the chemical bond in $A^{III}B^{V}$ compounds. Undoubtedly, solving this question also has a more general significance, since it can be extended to a broad class of compounds.

In order to obtain an unambiguous answer to the question posed above, in the present study we have undertaken an experimental determination of the magnitude and sign of the effective ionic charge of $A^{III}B^{V}$ compounds with the sphalerite structure from X-ray structural analysis data. In doing so, the following methods for determining effective ionic charges have been outlined and partially implemented.

First, the determination of the numbers of electrons belonging, respectively, to the ions A^{III} and B^{V} was carried out directly by counting from maps of the electron-density distribution constructed from X-ray diffraction data.

Second, the counting of the number of electrons belonging to each of the ions is carried out analytically from experimentally found values of the corresponding quantities A and α, entering into the expressions for the electron-density distribution in the predominantly inner part of the atom

Fig. 1. Electron-density distribution map in the (110) plane of the elementary cell of aluminum antimonide. The ion boundaries of Al and Sb are indicated by a dashed line.

$$\rho_1 = A_1 e^{-\alpha_1 r^2}$$

and the predominantly outer part of the atom

$$\rho_2 = A_2 e^{-\alpha_2 r^2}$$

([9,10]), with approximation of the electron-density distribution of the atom by two Gaussian functions

$$\rho = \rho_1 + \rho_2 = A_1 e^{-\alpha_1 r^2} + A_2 e^{-\alpha_2 r^2},$$

or by some other functions ([11,12]).

Third, the above counting was performed by comparing the values of the experimentally obtained structural amplitudes of the compounds with theoretical values calculated by Hartree—Fock and Thomas—Fermi methods for neutral atoms.

Fourth, the counting was performed on the basis of comparison of the experimentally determined structural amplitudes of the compounds with experimentally determined values of the structural amplitudes for the components—the elements forming the compounds.

The main results of the present investigation were obtained on the basis of the first and third methods.

Counting from the electron-density maps was carried out by graphical integration over a map drawn in the (110) plane. The ion boundaries were determined from the map. In doing so, spherical symmetry of the ions was assumed. As an example, Fig. 1 gives an electron-density distribution map on which the ion boundary is indicated by a dashed line. It should be noted that determination of the ion sizes from radii at a level below 0.03 el/Å^3 did not introduce any substantial difference into the magnitude of the ion charge. Table 1 gives the magnitudes of the effective charges of the ions of $A^{\mathrm{III}}B^{\mathrm{V}}$ compounds determined by the indicated method.

The calculation from the values of the structure amplitudes was carried out as follows. As is known, the square of the structure amplitude is

$$|F_{hkl}|^2 = \left\{ \sum_{ij} f_{ij} \cos 2\pi(hx + ky + lz) \right\}^2 + \left\{ \sum_{ij} \sin 2\pi(hx + ky + lz) \right\}^2 .$$

In the case of the sphalerite structure, for planes with even (h, k, l) indices whose sum is divisible by four, the structure amplitude is equal to the sum of the atomic scattering factors. For example, $|F_{400}| = |f_1 + f_2|$. For planes for which the sum of the indices is even but is not divisible by four, the structure amplitude is equal to the difference of the atomic scattering factors. For example, $|F_{200}| = |f_1 - f_2|$.

We carefully determined the absolute values of F_{200} for $A^{\mathrm{III}}B^{\mathrm{V}}$ compounds. The experimentally determined values of the structure amplitudes of the (200) line correspond to the actual difference of the atomic scattering factors of the ions of the $A^{\mathrm{III}}B^{\mathrm{V}}$ compound at the actually existing degree of ionization.

Table 1

Values of the effective charges of ions of $A^{\mathrm{III}}B^{\mathrm{V}}$ compounds (el.)

$A^{III}B^{V}$	From electron-density maps	From the Hartree-Fock F-factor	From the Thomas-Fermi F-factor
AlP	–	0.8 ± 0.20	0.32 ± 0.06
GaP	–	0.75 ± 0.20	0.62 ± 0.20
InP	–	(0.70) **	0.58 ± 0.15
AlAs	1.00 ± 0.25	0.60 ± 0.15	0.40 ± 0.08
GaAs	0.80 ± 0.22	0.51 ± 0.10	0.36 ± 0.07
InAs	0.49 ± 0.15	(0.50) **	0.35 ± 0.07
AlSb	0.67 ± 0.20*	(0.63) **	0.45 ± 0.08
GaSb	0.58 ± 0.17	(0.59) **	0.43 ± 0.07
InSb	0.38 ± 0.10	(0.27) **	0.18 ± 0.05

* The effective charge was determined for the antimony ion.

** Values obtained from comparison of the charge values calculated from the Thomas-Fermi F-factors and from the Hartree-Fock F-factors.

Since the sum of the squares of the indices of the (200) plane is comparatively small, i.e., the reflection angle is small, there is a proportionality between the ratio of the difference of the atomic scattering factors for neutral atoms of this plane and the experimentally observed difference (F_{200}), and the ratio of the difference of the atomic numbers of the component atoms ($Z_1 - Z_2$) to the actual difference of the electrons in the ions $\Delta x = x_1 - x_2$:

$$\frac{|f_1 - f_2|_{200}^{\text{neutr}}}{F_{200}^{\text{expt}}} = \frac{|Z_1 - Z_2|}{\Delta x}.$$

We did not have at our disposal all the experimentally obtained values of the atomic scattering factors of the component elements of $A^{III}B^{V}$. Therefore we took the values $|f_1 - f_2|_{200}^{\text{neutr}}$ for neutral atoms calculated by Thomas-Fermi and Hartree-Fock.

The magnitude of the effective charge of the ions e_{eff}, with allowance for the sign, was calculated from the relation

$$e_{\text{eff}} = \frac{|(Z_1 - Z_2) - \Delta x|}{2}.$$

Table 1 gives the values of the effective charges calculated by the indicated method from the experimental values of the structure amplitudes of the compounds and from the theoretically calculated values for neutral atoms according to Hartree-Fock and Thomas-Fermi.

Table 2 gives the experimental values of F_{200} obtained by us for the indicated $A^{III}B^{V}$ compounds.

Table 2

$A^{\mathrm{III}}B^{\mathrm{V}}$	AlP	GaP	InP	AlAs	GaAs	InAs	AlSb	GaSb	InSb
F_{200}	1.96	11.62	28.42	17.10	2.68	14.03	33.11	19.17	1.96

Thus, we have determined the effective charges for the antimonides, arsenides, and phosphides of aluminum, gallium, and indium. The magnitude of the effective charges is greatest for the phosphides and smallest for the antimonides. At the same time, the effective charges decrease in the series aluminum–gallium–indium. As

As established in the present study, the elements of the third group, A^{III}–metals–give up electrons and become positively charged ions, while the elements B^{V} accept electrons and become negatively charged ions. The redistribution of charge between the atoms under consideration constitutes a kind of polarization –a displacement of electron density from atoms of elements of the third group toward atoms–elements of the fifth group of D. I. Mendeleev' s periodic system.

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REFERENCES

1. E. Muser, V. Pirson, in *Semiconductor Substances*, IL, 1960.
2. J. C. Slater, G. F. Koster, Phys. Rev., **94**, 1499 (1954).
3. O. G. Folberth, Zs. Naturforsch., **15a**, 425 (1960).
4. W. G. Spitzer, N. Y. Fan, Phys. Rev., **99**, 1893 (1955).
5. D. A. Kleinman, W. G. Spitzer, Phys. Rev., **118**, 110 (1960).
6. G. Picus, E. Burstein et al., J. Phys. Chem. Solids, **8**, 282 (1959).
7. M. Hass, B. W. Henvis, J. Phys. Solids, **23**, 1099 (1962).
8. K. Khiltsum, A. Rose-Innes, *Semiconductors of the Type* $A^{III}B^{V}$, IL, 1963.

9. N. N. Sirota, N. M. Olekhnovich, A. U. Sheleg, DAN, **132**, 160 (1960).
10. N. N. Sirota, E. M. Gololobov, DAN, **138**, 162 (1961); **143**, 156 (1962); **144**, 398 (1962).
11. N. N. Sirota, DAN, **150**, 781 (1963).
12. A. I. Kitaigorodskii, *X-ray Structural Analysis*, 1950.

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