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Abstract

Full Text

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On the Nature of the Chemical Bond in Semiconductor Compounds $A^{III}B^{V}$

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According to the ideas of Mooser and Pearson ([1]), in $A^{III}B^{V}$ compounds the picture of bonding is the same as in elemental semiconductors of group IV, except that one electron from B^{V} passes to A^{III}. As a result, conditions are created for pairing s^2-electrons with subsequent sp^3-hybridization (Fig. 1). Thus, according to Mooser and Pearson, in $A^{III}B^{V}$ compounds the elements exhibit fourfold covalency and single electron valency. Already in this one respect, the nature of valence bonds in $A^{III}B^{V}$, according to ([1]), in fact differs sharply from that in elemental semiconductors of the germanium and silicon type.

The transfer of one electron from B^{V} to A^{III} also raises serious objections. In this connection the authors of ([1]) refer to Pauling ([2]), according to whom the transfer of an electron from a more electronegative atom to a more electropositive one is often encountered in intermetallic compounds and leads to their stabilization. These views of Pauling are based on his concept of electronic resonance, an analysis of which was made in ([3]). In fact, it is difficult to imagine the transfer of an electron from B^{V} to A^{III}. The electronegativity and ionization potential of the elements of the fifth group are greater than those of the metals of the third group. Consequently, in $A^{III}B^{V}$ one would rather expect the electron to tend to pass from A^{III} to B^{V}, and not the reverse.

Fig. 1. Valence scheme of bonds in $A^{III}B^{V}$ according to Mooser and Pearson

For an unambiguous solution of the question of the displacement of the electron cloud toward one or the other atom in $A^{III}B^{V}$ compounds, new experimental data are necessary. Among the few methods for independently determining the magnitude of the effective charge, infrared absorption in lattice vibrations is of interest. However, this method gives no information about the sign of the charges of the atoms ([4]). One of the direct methods for establishing the nature of the chemical bond is x-ray spectral analysis. It is known that, irrespective of the type of chemical bond, when it is formed a redistribution of electron density

Fig. 2 and Fig. 3: photometric curves of cadmium and antimony spectra

Figure 2: Fig. 2 and Fig. 3: photometric curves of cadmium and antimony spectra

takes place, as a result of which the affiliation of the outer electrons with the original atom changes. At the same time, the magnitude of the screening, by these electrons, of the inner electrons—to which x-ray spectra owe their origin—depends on the degree and character of the involvement of the valence electrons in the chemical bond. For this reason, x-ray spectra, which in principle reflect intra-atomic processes, are sensitive to the behavior of the valence electrons responsible for the chemical bond.

Modern advanced techniques for obtaining and studying x-ray spectra make it possible to detect the influence of the character of chemical bonds even on the deep-lying energy levels of elements. Nordling, Sokolowski, Zigbahn ([5]) and Fessler, Kremer ([6]) observed a shift of the x-ray spectral lines of copper and germanium toward the short-wavelength side in their oxygen compounds. We have shown a shift toward higher

energies of the zinc $K_{\alpha 1,2}$ lines in its semiconductor compounds with antimony (7). For illustration, in Fig. 2 we give our photometric curves of the cadmium $L_{\beta 15,2}$ band in the metal and in the compounds CdSb and Cd_4Sb_3. The shift of the indicated cadmium band in the compounds toward the short-wavelength side, in comparison with the metal, indicates that in the lattices of these substances excess positive charges are concentrated at the cadmium sites (7).

In the present work the principal attention is devoted to studying the shape and energy position of the antimony $L_{\beta 15,2}$ band in the metal and in the semiconductor compounds AlSb, GaSb, InSb, and CdSb.

The emission spectra of antimony were obtained on a Johann-type spectrograph from quartz crystals (0001) in first order of reflection. The dispersion in the region studied was 6.1 eV/mm, which corresponded to an accuracy in measuring each point of the spectrum on the microphotometer of ± 0.06 eV. To eliminate

Fig. 2. Photometric curves of the cadmium $L_{\beta 15,2}$-spectrum in compounds and in the metal

Fig. 3. Photometric curves of the antimony $L_{\beta 15,2}$-spectrum in compounds and in the metal

experimental errors that inevitably arise in measurements of this kind, the antimony $L_{\beta 15,2}$-spectrum in the compounds was recorded on the upper half of the film with the lower half covered, and then the same antimony spectrum in the metal was recorded on the lower half of the film. Next, on both halves of the same film the scandium reference line $1\,\mathrm{Sc}K_{\alpha 1}$ was recorded. Relative measurements were carried out within each film. For each substance three films were taken, the two best of which were photometered twice.

Figure 3 shows the antimony $L_{\beta 15,2}$-spectra in AlSb, GaSb, InSb, CdSb, and in the metal. The spectrum consists of two unresolved bands $L_{\beta 2}$ and $L_{\beta 15}$, corresponding to electron transitions $N_V \rightarrow L_{\text{III}}$ and $N_{IV} \rightarrow L_{\text{III}}$. The spectrum of metallic antimony has the simplest character, while those of AlSb and GaSb are complex. Here we shall not consider the fine structure of the spectra, which is a subject for separate discussion.

First of all, the shift of the antimony $L_{\beta 15,2}$ band in CdSb toward the long-wavelength side (Fig. 3) is noteworthy, whereas the same cadmium band in this same compound is shifted toward shorter wavelengths (Fig. 2). The shift of the maximum of the antimony $L_{\beta 15,2}$ band toward longer wavelengths (lower energy E) in AlSb, GaSb, and CdSb relative to the same band in the metal is due to the contraction of the electron cloud toward the antimony lattice sites of the indicated compounds. In this case the effective charge of the antimony nucleus decreases (as a result of increased screening by electrons drawn away from the cation-

former), as a result of which the $L_{\beta 15,2}$ band shifts toward the long-wavelength side.

Table 1 gives some data on the $L_{\beta 15,2}$ spectrum of antimony for antimonides of metals of the third group.

As is seen from the last column of the table, the shift of the maximum of the antimony $L_{\beta 15,2}$ band in the compounds AlSb and GaSb toward lower energy lies far beyond the limits of experimental error. On the basis of this fact, one may

Table 1

Compound	Electronegativity of atoms A^{III}	Total band width, eV	Distance between splitting maxima, eV	Shift of the principal maximum of the antimony $L_{\beta 15,2}$ band to the long-wavelength side relative to the metal, eV
AlSb	$1.5^{(8)}$	12.8	0.40	0.30 ± 0.06
GaSb	$1.6^{(8)}$	11.8	0.37	0.18 ± 0.06
InSb	$1.7^{(8)}$	9.8	not split	does not shift

categorically assert that in aluminum and gallium antimonides the valence electrons have a tendency to reside more at the antimony atoms than at Al and Ga.

Fig. 4. Scheme of chemical bonds in $A^{III}B^{V}$ compounds using AlSb as an example (according to the authors' data)

Figure 3: Fig. 4. Scheme of chemical bonds in $A^{III}B^{V}$ compounds using AlSb as an example (according to the authors' data)

Of course, this displacement of the electron cloud in $A^{III}B^{V}$ compounds toward B^{V} will be still more strongly expressed in the case of phosphides and arsenides. In this respect the antimony compounds prove to be the least suitable objects for x-ray spectroscopic investigations of this kind, since they require the greatest sensitivity of the experimental technique. Apparently for this reason InSb does not show a shift of the antimony $L_{\beta 15,2}$ spectrum. At the same time, InSb, in the series of antimonides, is the most covalent compound, as is indicated, for example, by the exceptionally high electron mobility and the small width of the forbidden band of this substance. The covalent character of the interatomic bond in InSb is indicated by the fact that the splitting of the antimony $L_{\beta 15,2}$ band is practically absent in it. In addition, the regular decrease in the total width of the band, measured with an accuracy of ± 0.5 eV, in going from AlSb to InSb (see Table 1) also indicates an increase in the degree of covalency in this series, which agrees well with the electrophysical characteristics of these substances. Finally, from aluminum to indium the electronegativity increases, as a result of which the electronegativity difference in InSb is minimal, i.e., this substance is the least ionic. Taken together, all this indicates that, in order to detect a displacement effect in InSb, if such an effect exists in it at all, methods of extremely high sensitivity are needed.

Fig. 4. Scheme of chemical bonds in $A^{III}B^{V}$ compounds using AlSb as an example (according to the authors' data)

Nevertheless, in the case of aluminum and gallium antimonides, on the basis of the shift of the antimony $L_{\beta 15,2}$ spectrum to the long-wavelength side, the absence of electron transfer from antimony to aluminum and gallium has been unambiguously proved. In this connection we propose a new scheme of tetrahedral covalent bonds in $A^{III}B^{V}$ compounds (using AlSb as an example), which is shown in Fig. 4. As is seen from the scheme, each atom (inside the dashed contour) is characterized by a completed electron octet. In this case the fourth electron pair, which forms the covalent bond, is supplied by the B^{V} atom from the undivided s^2 electrons. These electrons are shown in the scheme by bold dots.

Thus, of the four covalent bonds formed by each of the atoms A^{III} and B^{V}, one bond has a donor–acceptor origin, i.e., it is a coordinate bond ([9,10]).

For coordination lattices, which the compounds $A^{III}B^{V}$ are, the realization of one of the four bonds at the expense of a coordinate bond appears quite logical. At the same time, it should not be forgotten that a donor–acceptor bond differs from an ordinary covalent bond only in the origin of the bonding electron pair

and that, in the final result, they are completely identical. In classical chemistry one can find many analogous examples. Thus, nitrogen in the complex ammonium ion $[NH_4]^+$ forms a donor-acceptor bond with one of the hydrogens at the expense of an unshared $2s^2$-electron pair. As experimental data show, all four hydrogen atoms are completely equivalent in their chemical behavior, which is proof of the complete identity of covalent and coordinate bonds. The chemical analogues of nitrogen—phosphorus, arsenic, and antimony—are probably capable of forming coordinate bonds also in solids.

In the proposed bonding scheme of Fig. 4, the basic condition for the formation of binary compounds AB with tetrahedral coordination of the atoms in the structure is fulfilled: the average number of valence electrons per atom is equal to four. As for the shift of the $L_{\beta 15,2}$-spectrum of antimony toward lower energy, this is explained by the contraction of the electron clouds toward antimony owing to its greater electronegativity in comparison with Al. Therefore the lattice sites with aluminum have a δ^+-, and the antimony sites a δ^--charge, where $\delta \ll 1$.

The advantages of the proposed model of chemical bonds in $A^{III}B^{V}$ appear still more clearly when considering the semiconductor compounds $A^{II}B^{VI}$ and $A^{I}B^{VII}$, which likewise crystallize in the zinc-blende structure. According to Mooser and Pearson, in order to form tetrahedral bonds in $A^{II}B^{VI}$, the atoms B^{VI} must give two electrons to the atoms A^{II} and become doubly positively charged. In the compounds $A^{I}B^{VII}$, for example CuI, iodine must give copper as many as three electrons before sp^3-hybridization occurs, with the subsequent formation of covalent bonds. All this does not fit within the framework of the usual concepts of chemistry and is unlikely to occur in reality. It is considerably simpler and, undoubtedly, more correct to assume the presence in the compounds $A^{II}B^{VI}$ and $A^{I}B^{VII}$, respectively, of two and three coordinate bonds, where elements of groups VI and VII of the periodic system function as complex-formers.

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References Cited

1. E. Mooser, W. B. Pearson, *J. Electronics*, **1**, 629 (1956).

2. L. Pauling, *Proc. Nat. Acad. Sci. U.S.A.*, **36**, 533 (1950).

3. *The State of the Theory of Chemical Structure in Organic Chemistry.* Report of the Commission of the Division of Chemical Sciences, Academy of Sciences of the USSR, Moscow, 1954.

4. K. Hilsum, A. Rose-Innes, *Semiconductors of the $A^{III}B^{V}$ Type*, Foreign Literature Publishing House, 1963, p. 31.

5. C. Nordling, F. Sokolowski, K. Siegbahn, *Arkv. fys.*, **13**, 37, 495 (1959).

6. A. Faessler, H. Krämer, *Ann. Phys.*, **4**, 1-5, 263 (1959).

7. Ya. A. Ugai, E. P. Domashevskaya, T. A. Marshakova, *Journal of Structural Chemistry*, **4**, 250 (1963).

8. S. S. Batsanov, *Electronegativity of Elements and the Chemical Bond*, 1962, p. 65.

9. B. V. Nekrasov, *Course of General Chemistry*, Moscow, 1952, p. 353.

10. A. A. Grinberg, *Introduction to the Chemistry of Complex Compounds*, 1945, p. 239.

Note: Figure translations are in progress. See original paper for figures.