ELECTRON DENSITY AND CHEMICAL BONDING IN TETRAGONAL A$_2$B$_5$ CRYSTALS. I. CdAs$_2$

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The band structure and electron density $\rho(r)$ have been calculated for tetragonal CdAs$_2$. The lower subband of the valence band corresponds to the s-like states of arsenic atoms. The upper subband corresponds to the p-states forming bond charges. The electron density maxima are located in the middle of the bond between the neighbors in the spiral chain of arsenic atoms. Between the nearest cadmium and arsenic atoms there is also the maximum $\rho(r)$ shifted from the center of the bond toward the arsenic atom. Thus, the bond in the chain is of a clearly covalent character, while the Cd–As bond is covalent, with a contribution of the ionic term.

The A$_2$B$_5$ semiconductors crystallize in different structure modifications and possess interesting practical properties. By now, optical, electric, thermoelectric, and physicomechanical properties have been investigated for many compounds of the A$_3$B$_5$ group. In particular, for CdAs$_2$ crystals, the conductivity and the Hall constant have been measured; effective masses of electrons and holes have been measured by cyclotron resonance; reflection spectra have been recorded; and the absorption edge has been analyzed. Recent studies were generally performed for oriented crystals, for which dispersion of the refractive and birefringence indices and the tension resistance effect have been measured. The high tension-resistant properties of CdAs$_2$ crystals are of practical interest for use in strain measurement technology. The electric conductivity and the Hall constant have been examined for oriented crystals in the temperature range from 77 to 400 K. The CdAs$_2$ crystals were found to possess a high anisotropy of electric properties [1-3]. The above experiments have stimulated detailed theoretical calculations of the band structure and chemical bond parameters in CdAs$_2$ crystals.

BAND STRUCTURE OF CdAs$_2$

The band structure calculations used the crystal structure data of [4]. The notation for symmetric points of the Brillouin zone is the same as in [5]; the notation of small irreducible representations used in the calculation follows [5] but the numbering of representations is preserved as in [6].

The band structure calculations were performed taking into account spin-orbital coupling in the main symmetric points and directions, as well as in some special points of the Brillouin zone. Spin-orbital coupling was included in the calculation by Weisz' method [7]; the parameters of atomic spin-orbital splittings for Cd and As were taken the same as for CdSnAs$_2$ [8], with an appropriate renormalization to the unit cell volume of CdAs$_2$. The form factors of atomic pseudopotentials were taken from [3] and were slightly varied to get the experimental $E_g$ value without changing the band topology.

The expansion of the pseudowave function was carried out taking into account $\sim 340$ spin orbitals. Using the basis of symmetrized combinations of plane-wave spinors has made it possible to reduce the order of the secular equation by a factor of two in directions $\Delta$, $R$, $D$, $A$, and $\Sigma$ and by a factor of four in direction $A$.

The calculated band structure of CdAs$_2$ is shown in Fig. 1. The valence band of CdAs$_2$ contains two subbands separated by a significant energy gap $\Delta E \sim 3$ eV. Spin-orbital coupling introduces considerable changes only in the points $\Gamma$, $T$, and $P$ where some valence band levels of symmetry $\Gamma_5$, $T_5$, and $P_1$ split to $\sim 0.13$-0.25 eV. The splitting...
values in the points \( N, L \) and on the lines are \(< 0.05 \text{ eV} \). The top of the valence band and the bottom of the conduction band of \( \text{CdAs}_2 \) are found in the \( T \) point of the Brillouin zone; consequently, the absorption edge in this crystal should be straight. The conduction band is simple: the nearest additional minimum lies in the \( N \) point at a distance of \(-1.8 \text{ eV} \) from the bottom of the band. The nearest additional maxima of the valence band in the \( P \) and \( L \) points are \(-0.5 \text{ eV} \) away from the top.

**METHOD OF CALCULATION OF VALENCE ELECTRON CHARGE DISTRIBUTION**

The valence electron charge distribution \( \rho(r) \) in crystals may be calculated if we know the wave functions of the valence states (or the filled states of the conduction band in metals) \( \psi_{nk}(r) \) found from the band calculations. In this case (neglecting the spin-orbital coupling),

\[
\rho(r) = \frac{2eN}{\Omega_{BB}} \sum_n \int [\Psi_{nk}(r)]^2 d^3k, \tag{1}
\]

where integration and summation are done over all the filled states; \( \Omega_{BB} \) is volume of the Brillouin zone; \( N \), the number of unit cells in volume \( V \) of the crystal; and \( e \), the electron charge.

The direct computation of integral (1) requires enormous computer time. For rough calculations of \( \rho(r) \), the special points method is generally used [9]. To apply this technique to \( \text{CdAs}_2 \), the integrand function in (1) should be symmetrized with respect to \( K \) over the point group \( G_0 = D_4 \):

\[
\bar{f}(K) = \frac{1}{|G_0|} \sum_{\hat{R} \in G_0} |\psi_{n,\hat{R}K}(r)|^2 = \frac{1}{|G_0|} \sum_{\hat{R} \in G_0} |u_{n,\hat{R}K}(r)|^2, \tag{2}
\]

where \( \bar{f}(K) \) is the function obtained by symmetrization; \( u_{n,\hat{R}K}(r) \), the periodic part of the Bloch function \( \psi_{n,K}(r) \); \( \hat{R} \), an element of group \( D_4 \); \( |G_0| \), the number of elements in \( G_0 \); and \( \hat{R}_K \), the wave vector derived from \( K \) after the point transformation of \( \hat{R} \) from \( G_0 \). Taking into account that

\[
u_{n,\hat{R}K}(r) = u_{n,K}(g^{-1}r), \tag{3}
\]

where \( g = (\hat{R}/\tau_R) \) is the main element of the space group consisting of the point element \( \hat{R} \) and the corresponding