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An Electronic Band Structure Calculation and the Optical Properties of Alkaline–Earth Sulphides

By

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The electronic band structure of CaS, SrS, and BaS is calculated by linear augmented plane waves (LAPW). The calculation is applied for the explanation of the optical properties of the alkaline-earth-metal sulphides.

Die elektronische Bandstruktur von CaS, SrS und BaS wird mit der LAPW-Methode berechnet. Die Rechnung wird für die Erklärung der optischen Eigenschaften der Erdalkali-Sulphide benutzt.

1. Introduction

A^2B^6 compounds have a great importance both in view of pure science and of technology due to their extraordinary physical properties. Some of the alkaline-earth sulphides (e.g. CaS, SrS, BaS, etc.) are excellent photo, X-ray, and cathode luminophors, having a bright glow, a great capacity, and a bright IR radiation. These properties of alkaline-earth sulphides are widely used in optics, optoelectronics, television engineering, etc.

Some of the physical properties of these compounds cannot be explained without a detailed study of their electronic structure. The existing experimental and theoretical works on A^2B^6 [1 to 6] compounds are contradictory in some respects. As is known, a systematic theoretical investigation of the optical behaviour of A^2B^6 compounds has not yet been done. Recently, the electronic band structure of CaS has been calculated [6] from first principles.

Our aim in the present paper is to calculate the electron energy band structure of CaS, SrS, and BaS, based on their optical spectra. The experimental investigations of these compounds are extremely difficult because of their extraordinary chemical activity [5]. One of the most effective methods is the ab initio self-consistent calculation, including the scalar relativistic effects.

In Section 2 a brief description of the calculation procedure and the list of the main parameters of energy band structure for CaS, SrS, and of BaS are given. The discussion of optical properties of the compounds is given in Section 3.

2. Calculation of the Electronic Band Structure

The approximation was carried out by use of the self-consistent linear augmented plane wave (LAPW) method [7] in the frame of the electron density functional theory [8].

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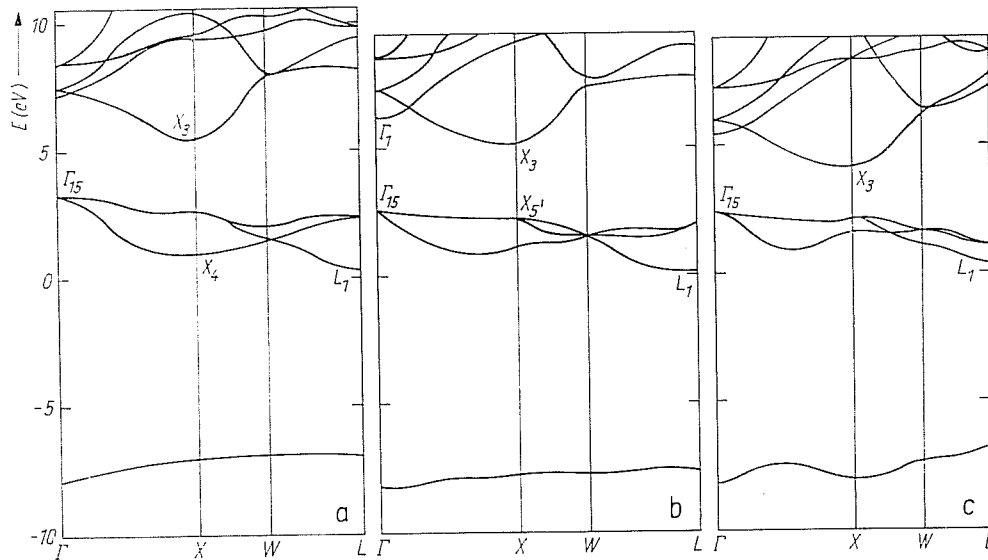[3]) SU-294693 Voronezh, USSR.

Fig. 1. Energy band structure of a) CaS, b) SrS, and c) BaS

The self-consistent electronic structure calculation with the LAPW method in scalar relativistic approximation has been presented in this paper. In this approximation the high components of the wave function have been considered only.

The self-consistency was given at 19 points of the irreducible part of the Brillouin zone. The accuracy of electron density is better than 1%, while the accuracy of electron energy eigenvalues is 0.014 eV. The electronic band structure and the corresponding wave functions were computed in 89 points of the irreducible part of the Brillouin zone. The electronic energy band structures of CaS, SrS, and BaS are presented in Fig. 1 a to c.

A lower valence band appearing in the compounds investigated is formed by s-states; while the upper valence band is created by p-states of the anion. The top of the valence band is located at the Γ_{15} symmetry point, while the bottom of the conduction band is formed by d-states of the cation, located at the X_3 symmetry point. Thus CaS, SrS, and BaS are typical indirect band dielectrics. The characteristic values of the energy band structures of the given compounds are collected in Table 1. It is

Table 1

The calculated data of the given compounds

	CaS	SrS	BaS
	energy (eV)		
Γ_{15}-Γ_1	3.936	3.508	3.261
X_5-X_3	2.950	2.782	2.044
Γ_{15}-X_3	2.143	2.298	1.821
Γ_{15}-L_1	3.161	2.578	2.148

well observable from the data that by increasing the atomic number of the cation, the direct gap width decreases. This tendency is obvious from the decreasing excitation energy with increasing atomic energy quantum number. The width of the indirect band gap (determined by energy difference at Γ_{15} and X_3 states) non-monotonically depends on the atomic number.

It seems that the charge distribution in the system can be approximated with high accuracy by the self-consistent calculation. Ionicity estimated in terms of [9] is $+0.5$, $+0.65$, and $+0.73$ for Ca, Sr, and Ba, respectively. The increase of the growth of ionicity versus atomic number for the cations is explained by the decrease of ionization potential.

3. Optical Properties

The imaginary part of dielectric permittivity function was calculated in terms of the formula as follows [10]:

$$\varepsilon_2(\omega) = \frac{4\pi^2 e^2}{m^2\omega^2} \sum_{v,c} \int \frac{2\,\mathrm{d}\boldsymbol{k}}{(2\pi)^3} \, |e\varrho_{cv}(\boldsymbol{k})|^2 \, \delta(E_c - E_v - \hbar\omega) \,, \tag{1}$$

where

$$\varrho_{cv}(\boldsymbol{k}) = \langle \psi_c(\boldsymbol{k}) | -i\nabla | \psi_v(\boldsymbol{k})\rangle \,.$$

This means that the energy dependence of matrix elements of optical transitions is calculated in the frame of self-consistent LAPW for A^2B^6 compounds.

Generally this energy dependence was neglected [10]; however, the essential importance of this effect has been pointed out [11] in the case of A^2B^6 compounds.

The eigenvalues in the frame of the electron density functional are determined from

$$\left(-\frac{\hbar^2\nabla^2}{2m} + V_{\mathrm{eff}}(\boldsymbol{r})\right)\tilde{\psi}_i = \tilde{E}_i\tilde{\psi}_i \,; \tag{2}$$

$$V_{\mathrm{eff}}(\boldsymbol{r}) = V_{\mathrm{ext}}(\boldsymbol{r}) + V_{\mathrm{H}}(\boldsymbol{r}) + V_{\mathrm{xc}}(\boldsymbol{r}) \,. \tag{3}$$

The energies $\tilde{E}_i$ have no direct physical meaning. The excitation energies by quasi-frequencies are calculated from the poles of the corresponding Green function appearing in the Dyson equation,

$$\left(-\frac{\hbar^2\nabla^2}{2m} + V_{\mathrm{ext}}(\boldsymbol{r}) + V_{\mathrm{H}}(\boldsymbol{r})\right)\psi_i(\boldsymbol{r}) + \int \mathrm{d}^3r' \, \Sigma_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}', E_i) = E_i\psi_i \,, \tag{4}$$

where $\Sigma_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}', E_i)$ is a nonlocal energy-dependent operator.

The value of $(E_i - \tilde{E}_i)$ is weakly dependent on the energy at the conduction band of these dielectrics [12, 13] in the approximation shown in (4). The wave functions $\psi(\boldsymbol{r})$ and $\tilde{\psi}(\boldsymbol{r})$ are practically identical, hence there is a rigid shift of the conduction bands. This is practically equivalent with the shift of the $\varepsilon_2(\omega)$ spectrum. The spectra approximated in the above-described calculation are generally agreeing well with the experiments of [5]. A comparison of recent theoretical and experimental [5] spectra for CaS, SrS and BaS are shown in Fig. 2. Only for the compound BaS the calculation does not agree with the experiment. The theoretical spectra were obtained by rigid shifting of the spectra by the value ΔE_g calculated from (1). ΔE_g is an underestimated width of the band gap.

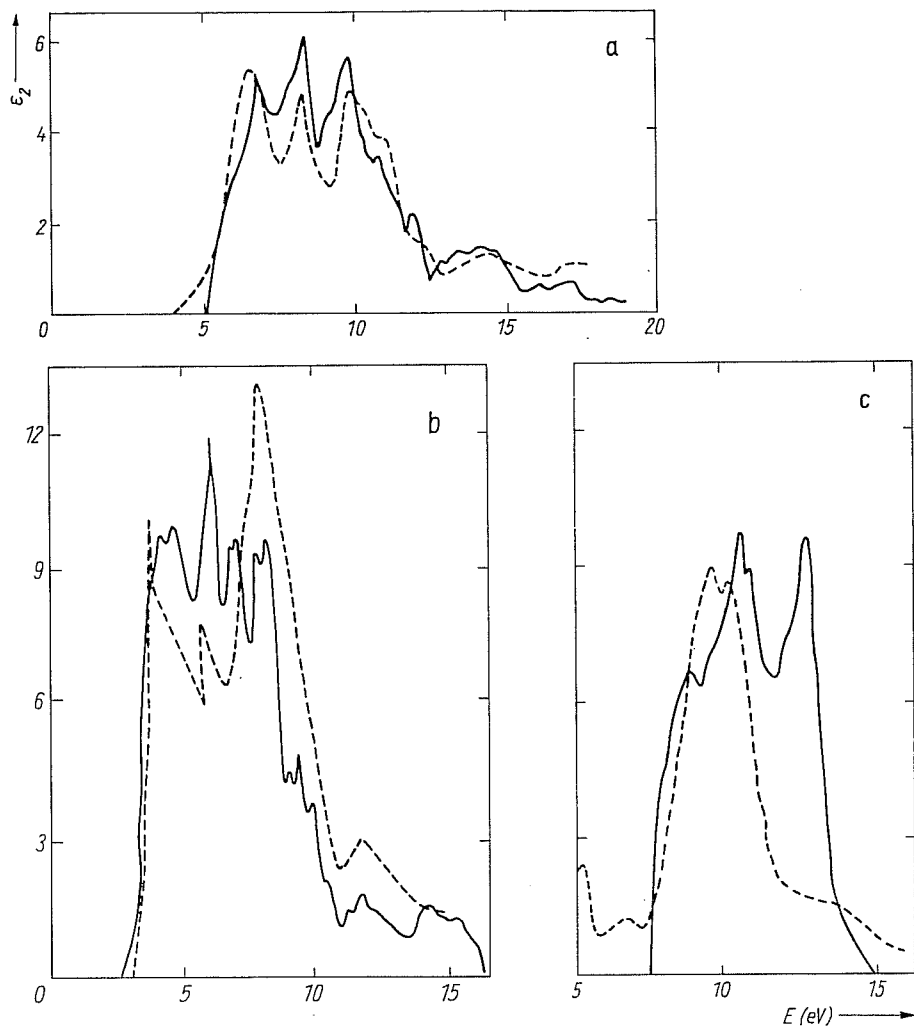The details of the optical spectra are analysed in the following.

Fig. 2. Imaginary part of the dielectric permittivity function. – – – experiment [5], ——— present theory. a) CaS, b) SrS; c) BaS

3.1 CaS

The first peak consists of the transition in the vicinity of the Γ-point of the Brillouin zone as $\Gamma_{15} \to \Gamma_{25}$, $\lambda_3 \to \lambda_1$, $\Sigma_4 \to \Sigma_2$, $\Delta_5 \to \Delta_2$.

The second peak is built up by transitions at the L-point as, e.g. $L_3 \to L_2'$, $Q_1 \to Q_2$.

The third one is formed by transitions to the ΓXWK-plane.

3.2 SrS

The first peak is constructed by $K_4 \to K_1$, $U_4 \to U_1$, $\Delta_1 \to \Delta_5$, and all the transitions to the plane ΓXWK.

The second peak is characteristic of $\Delta_2' \to \Delta_2$, $\Sigma_3 \to \Sigma_1$, $Q_1 \to Q_1$, $\Delta_1 \to \Delta_1$, $W_3 \to W_1$, $Q_1 \to Q_2$, and the transitions to the plane ΓKL.

Table 2

The values of the theoretical shifts ΔE_g and the corresponding atomic number of the metallic component

	CaS	SrS	BaS
	energy (eV)		
ΔE_g	1.75	2.1	3.0
Z_m	20	38	56

The third peak is built up by $\Delta_2' \rightarrow \Delta_5$ and transitions to ΓXWK

The fourth peak is also formed by $\Delta_2' \rightarrow \Delta_5$, $\Delta_5 \rightarrow \Delta_5$, $\Sigma_4 \rightarrow \Sigma_1$, and transitions to ΓXWK.

3.3 BaS

The first peak is consisting the transitions $\Gamma_{15} \rightarrow \Gamma_{25}'$, $\Delta_1 \rightarrow \Delta_1$, $\lambda_3 \rightarrow \lambda_1$, $\Sigma_1 \rightarrow \Sigma_1$, $\Sigma_4 \rightarrow \Sigma_2$, $\Sigma_3 \rightarrow \Sigma_3$, $K_4 \rightarrow K_1$.

The second (double) peak is formed by $\Delta_5 \rightarrow \Delta_2$, $\lambda_1 \rightarrow \lambda_3$, $\lambda_3 \rightarrow \lambda_1$, $\Sigma_1 \rightarrow \Sigma_4$, $\Sigma_3 \rightarrow \Sigma_1$, $\Sigma_1 \rightarrow \Sigma_3$.

The third appears from the transitions $W_3 \rightarrow W_2'$, $\Delta_5 \rightarrow \Delta_1$, $\Delta_1 \rightarrow \Delta_5$, $\Delta_5 \rightarrow \Delta_5$, $\lambda_3 \rightarrow \lambda_3$, $\Sigma_1 \rightarrow \Sigma_4$, $\Sigma_3 \rightarrow \Sigma_1$, $K_3 \rightarrow K_2$.

The values of theoretical shifts ΔE_g and the atomic numbers of metallic elements in the given compounds (Z_m) are listed in Table 2. The trend in ΔE_g is monotonic, their dependence on Z_m is well linear.

4. Conclusion

The calculation of electronic energy band structure and optical spectra for CaS, SrS, and BaS was performed by the self-consistent LAPW method. The sulphides are dielectrics of with indirect band.

The most important parameters of the band structure were obtained. The calculation procedure used describes the spectrum $\varepsilon_2(\omega)$ for CaS and SrS in good agreement with experiment.

The good correspondence of our calculations with the experimental observations for compounds CaS and SrS is weakened by the unsatisfactory agreement in the case of BaS. Up to now only one experimental spectrum is available for the comparison with our recent theory for the compound BaS [5]. Because of the extremely high chemical activity in oxidation of BaS, we suggest a remeasuring program for experimental laboratories clarifying this problem.

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