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Electronic Structure and Optical Properties of MgS

By

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The electronic structure and optical properties of MgS are calculated by the totally self-consistent linear augmented plane wave method.

Elektronenstruktur und optische Eigenschaften von MgS werden mit der vollständig selbstkonsistenten LAPW-Methode berechnet.

1. Introduction

Alkaline-earth metal sulfides are important in several practical applications as X-ray, photo and cathode-ray luminophors. They are actively investigated both theoretically [1 to 3] as well as experimentally [4 to 6]. The band structures and optical spectra of CaS, SrS, and BaS have been obtained but there is very little information about MgS. Only the partial effects of exchange-correlation and Coulomb energy were studied [7] in the frame of electron density functional theory. In our present paper, the electronic structure of magnesium sulfide was obtained by the fully self-consistent linear augmented plane wave (LAPW) method [8] within the frame of electron functional density theory [9]. The potential of exchange correlation was constructed by the local density approximation. Consequently, the investigation of the electronic structure of MgS and its optical properties is interesting and up to date a task for a full description of alkaline-earth metal sulfide properties.

2. Results

The calculated band structure of MgS is given in Fig. 1. The upper limit of the valence band is at point Γ_{15} and the bottom of the band is situated at the point L_1. This band is created by p-states while the bottom of the valence band is created by s-states of sulphur. The lowest point of conduction band is found at point X_1. It is created by s-states of Mg and to a lower degree by d-states of S. It should be mentioned that in all investigated alkaline-earth metal sulfides (CaS, SrS, and BaS) [1 to 3] the point X_3, created by d-states of the cation is found lower in energy than the point X_1. This is caused by the fact that excited d-states of Mg are much higher than those of other alkaline-earth metals. Consequently the point X_3 is created basically by d-states of S which has been lowered but not enough to form the bottom of the conduction band. Basic energy characteristics of the band structure are listed in Table 1.

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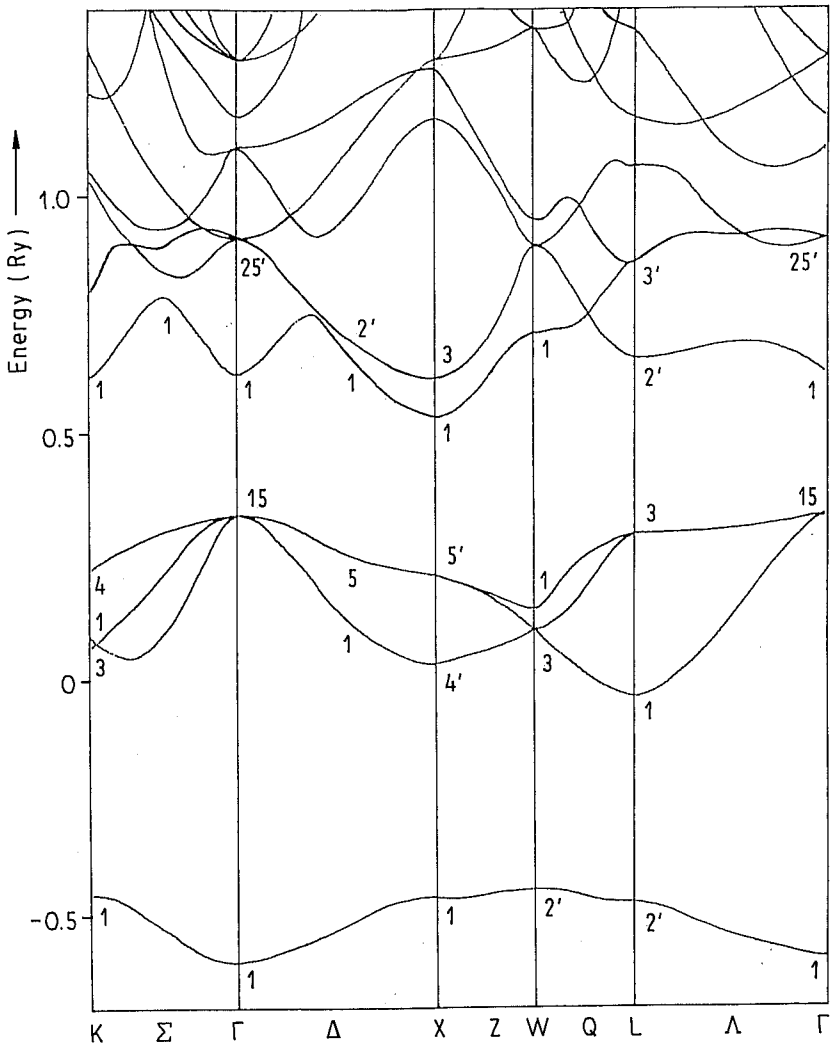

Fig. 1. Calculated band structure of MgS

Table 1
Basic energy characteristics of the band structure of MgS

	E (eV)
E_g (Γ_{15}-Γ_1)	3.94
E_g (X_5-X_1)	4.33
E_g (Γ_{15}-X_1)	2.69
E_v (Γ_{15}-L_1)	5.08
E_v (Γ_{15}-$X_{5'}$)	1.64
E_c (Γ_1-$X_{1'}$)	1.25

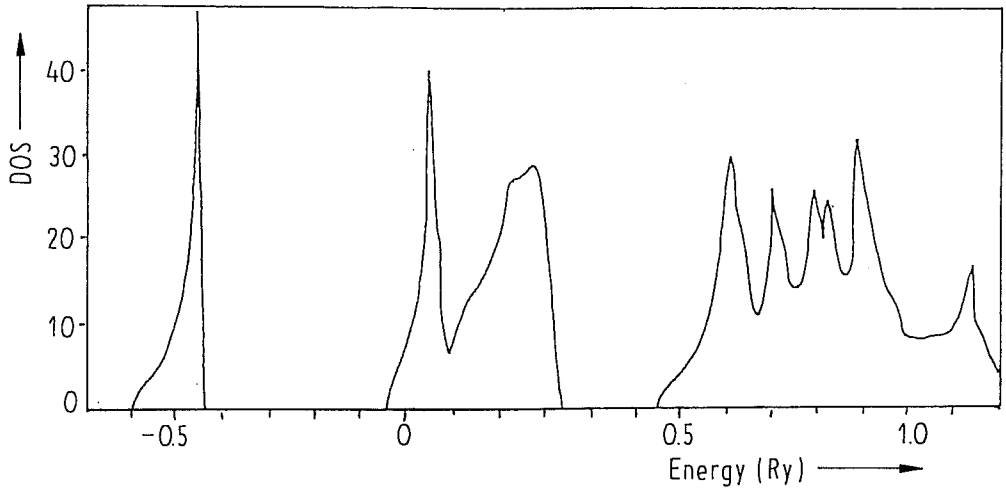

Fig. 2. Calculated density of states (in arb. units) for MgS

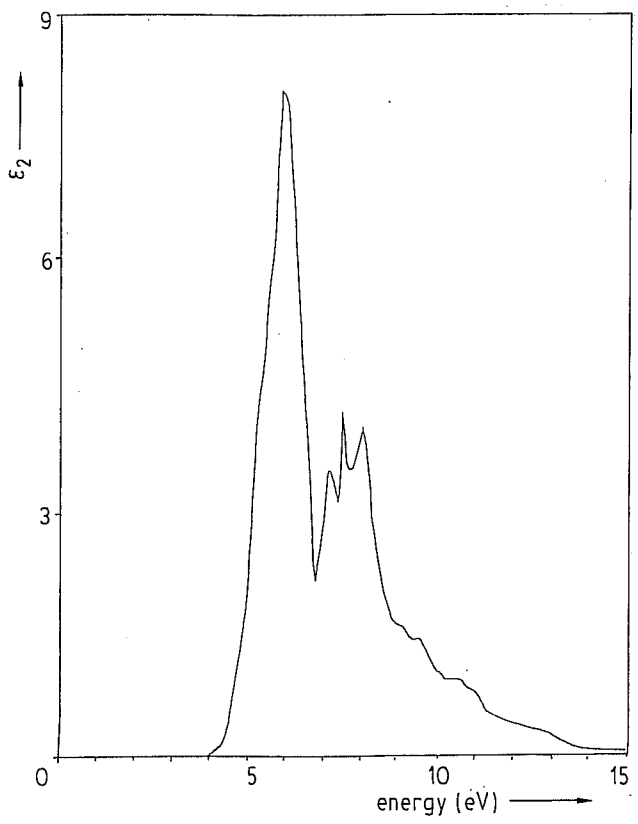

Fig. 3. Spectra of $\varepsilon_2(\omega)$ for MgS

The calculated density of states is shown in Fig. 2. A substantially detailed structure of the conduction band has been obtained, the peaks in the conduction band have the same magnitude as those in the valence band. There is a doublet character of the density of states in the valence band.

On the basis of the electronic structure of MgS calculations were provided for the imaginary part of the dielectric function ($\varepsilon_2(\omega)$),

$$\varepsilon_2(\omega) = \frac{4\pi^2 e^2}{m^2\omega^2} \sum_{v,c} \int 2dk/(2\pi)^3 \, |eM_{c,v}(k)|^2 \, \delta(E_c - E_v - \hbar\omega),$$

where the matrix elements $M_{c,v}(k) = \langle \Psi_c | - i\hbar\nabla | \Psi_v \rangle$ have been calcuated by the LAPW method [2, 3].

In the spectrum of $\varepsilon_2(\omega)$ (Fig. 3) the first peak is created by transitions from the p-state of S to the s-state of Mg and to the d-state of S in the conduction band. These transitions are found in points of general positions in the Brillouin zone. The second peak (at an energy of 6.85 eV) corresponds to transitions $\Delta_1 \rightarrow \Delta_2$ near the point X. The third peak (at 7.48 eV)

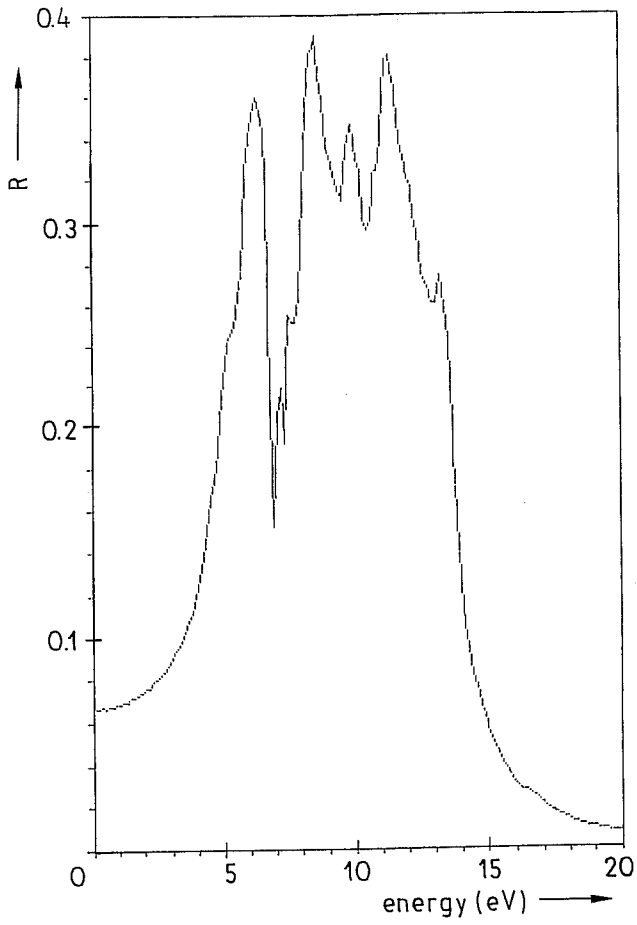

Fig. 4. Reflection coefficient for MgS

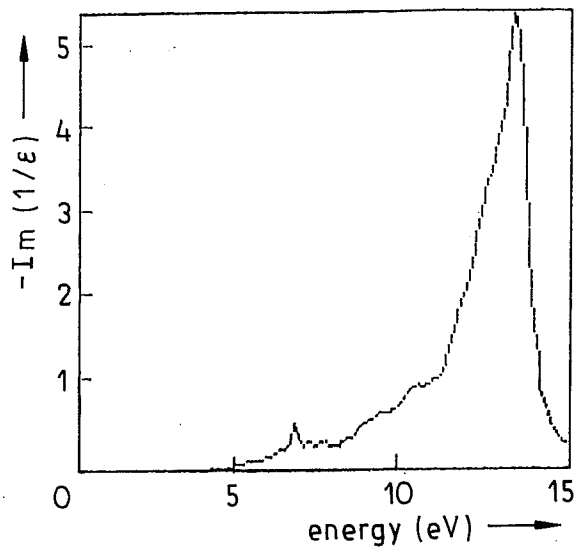

Fig. 5. Characteristic loss function of MgS

refers to $L_3 \rightarrow L_{3'}$, and $\Delta_5 \rightarrow \Delta_{2'}$, transitions are in the vicinity of point Γ. The fourth peak (8.03 eV) corresponds to transitions $\Delta_5 \rightarrow \Delta_{5'}$, in the vicinity of the Γ-point connected with the transition from the top of the valence band into d-states of sulphur. Due to the relatively under-estimated value of the band width of the gap in the theory of electronic density functionals compared to the experimental $\varepsilon_2(\omega)$ spectra a correction of calculated values has to be done. For example, based on our experience with dielectric materials a constant rigid shift of the whole calculated spectra can correct the under-estimated band width, [2, 3]. In Fig. 4, the reflection coefficient $R(\omega)$ calculated by the Kramers-Kronig relation is given.

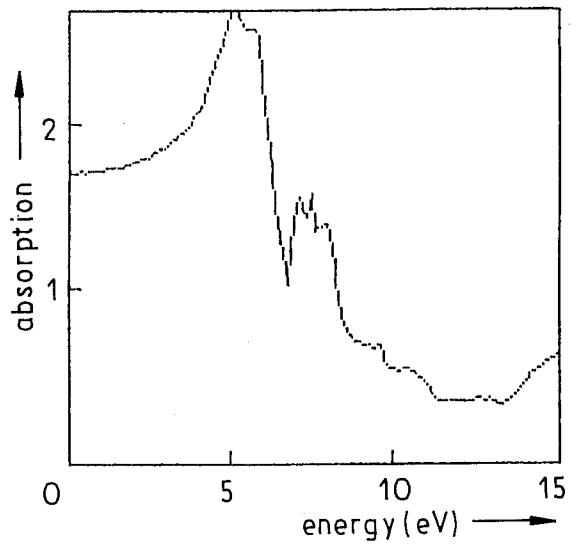

Fig. 6. Absorption of MgS

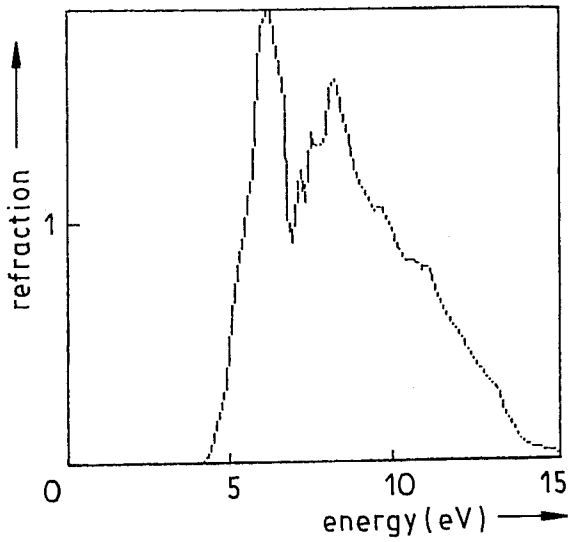

Fig. 7. Refraction of MgS

A decrease of the reflection coefficient for photons having energy higher than 15 eV is observable.

We have calculated the plasma frequency (ω_p) of magnesium sulfide as well. From the free-electron approximation ω_p has been found as 8.87 eV. However, a more accurate excitation energy of plasmons was obtained by calculating the characteristic loss function $-\mathrm{Im}(1/\varepsilon(\omega))$ (Fig. 5). Not all maxima of the characteristic loss function correspond, however, to an excitation of plasmons, it is necessary to fulfil the conditions: $\varepsilon_1(\omega) = 0$ and $\varepsilon_2(\omega) \ll 1$. From these conditions the value of $\omega_p = 12.69$ eV was obtained. We calculated also such optical parameters of MgS as absorption and refraction coefficients, Fig. 6 and 7, respectively. Maximum absorption is observed in the energy range of 5 to 10 eV which means that there are interband transitions. The results obtained can be used for an experimental investigation of such compounds in the future.

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