

phys. stat. sol. (b) 171, K23 (1992)

Subject classification: 71.25; S8; S10.1

Department of Solid State Physics,
Lomonosov State University, Moscow¹⁾ (a)
and Department of Atomic Physics, Eötvös University, Budapest²⁾ (b)

Electronic Structure of MgO and SrS Compounds under Pressure

By

V.S. STEPANYUK (a), A. SZASZ (b), A.A. KATSNELSON (a),
A.A. GRIGORENKO (a), and O.V. FARBEROVICH (b)

Introduction The alkaline earth metal sulfides and oxides are widely used both in science and technology. In recent years a number of works were made on the electronic structure of various representants of these compounds /1 to 3/. Their optical properties have been studied /2, 3/, within the framework of the electronic density functional theory /4/. The experimental spectra were successfully described in details.

A series of alkaline-earth metal compounds (MgO, CaO, BaO) have a NaCl-CsCl-type phase transformation under pressure. Hence, the study of the changes of the electronic structure versus the pressure is inevitably important. This question has not been investigated except for MgO /5/, and very recently a work was published for CeS /6/. Furthermore the calculation of the optical properties of MgO and SrS systems under pressure changes was not attempted at all.

In our present work the electronic structure and optical properties of MgO and SrS compounds under hydrostatic pressure are discussed.

Calculation method Electronic structure of MgO and SrS (in normal and compressed state) was calculated by the self-consistent linear augmented plane waves (LAPW) method /7/ within the framework of the electronic density functional theory in 89 points of the irreducible part of the first Brillouin zone. The applied Khon-Sham potential of the exchange-correlation has been calculated by the local density approximation. The self-consistency was reached when the electron density for the preceding iteration differed from the electron density of the next one by 1 % and eigenvalues changed by not more than 0.005 Ry.

Further, the density of states was calculated by the tetrahedron method /8/. The imaginary part of the dielectric function $\epsilon_2(\omega)$ is given by /9/

$$\epsilon_2(\omega) = (4\pi^2 e^2 / m^2 \omega^2) \sum_{v,c} \int \frac{2dk}{2\pi^3} |eM_{c,v}(k)|^2 \delta(E_c - E_v - \hbar\omega) ,$$

¹⁾ Lenin Hills, 117234 Moscow, Russia.

²⁾ Muzeum krt. 6 to 8, H-1088 Budapest, Hungary.

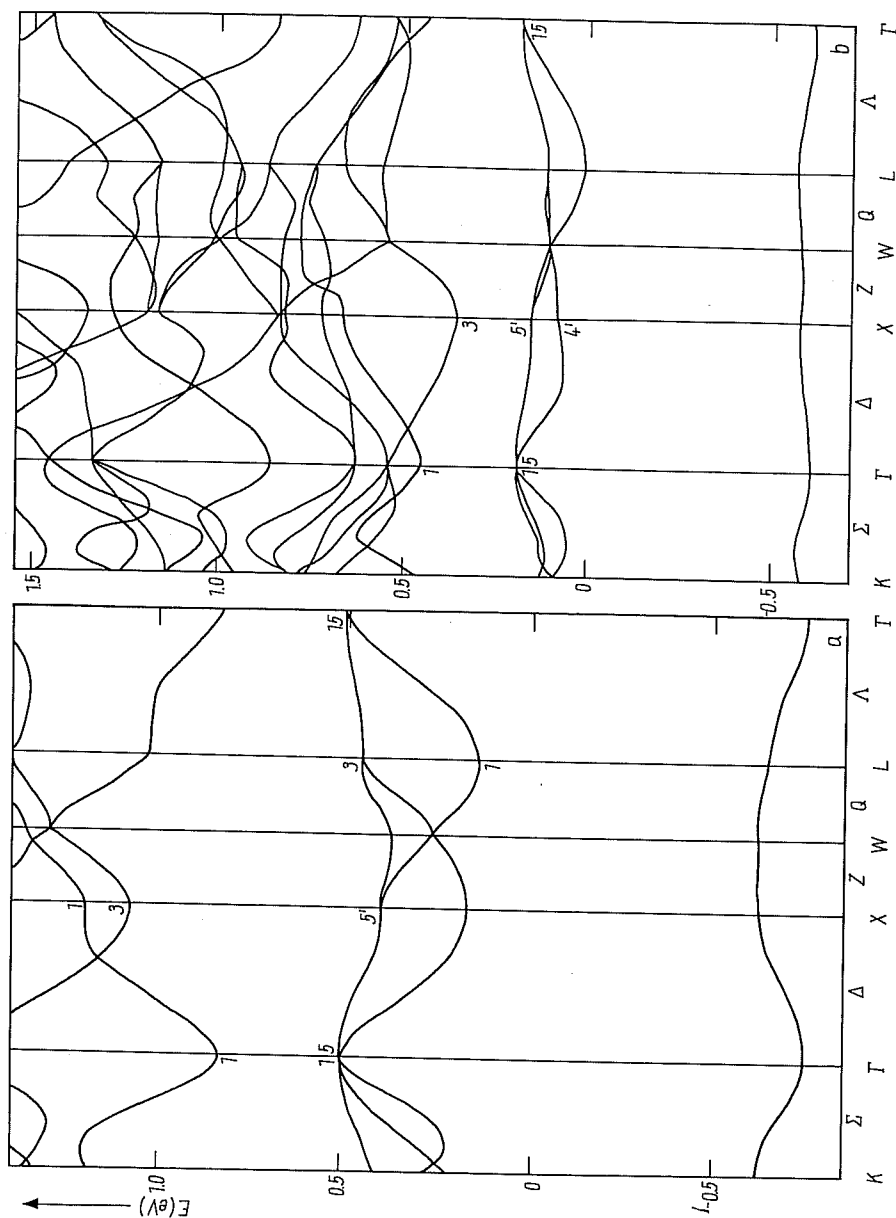


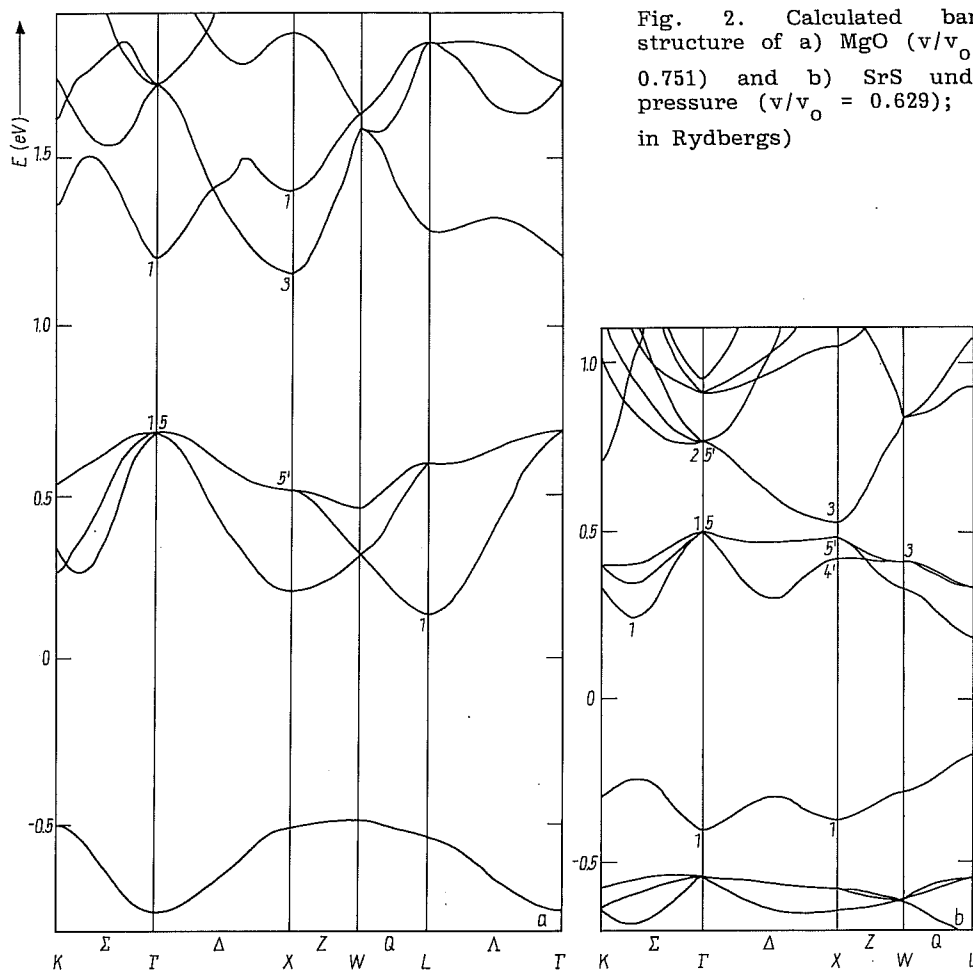
Fig. 1. Calculated band structure of a) MgO and b) SrS in normal state (E in Rydbergs)

where

$$M_{c,v}(k) = \{ \psi_c(k,r) | \nabla | \psi_v(k,r) \} .$$

The matrix elements were constructed from LAPW functions. For LAPW calculation a MT potential was used, and so the matrix elements have to be calculated inside and outside the MT sphere.

Fig. 1. Calculated band structure of a) MgO and b) SrS in normal state (E in Rydbergs)

Fig. 2. Calculated band structure of a) MgO ($v/v_0 = 0.751$) and b) SrS under pressure ($v/v_0 = 0.629$); (E in Rydbergs)

The band structure of MgO and SrS in the equilibrium state is shown in Fig. 1a and b. The lower part of the valence band is due to s-states while the upper part of the band to the p-states of the anions. In MgO the bottom of the conduction band is due to the s-states of Mg, and in SrS - to d-states of Sr. It is worth noting that MgO itself is a direct band dielectric and SrS is an indirect one.

The contractions of the lattice parameters for MgO and SrS by hydrostatic pressure were given as $v/v_0 = 0.751$ relative volume per atom (approximately 10^{12} Pa) and $v/v_0 = 0.629$, (approximately 10^{10} Pa), respectively. These values were chosen for the following reasons:

- the $\Gamma \rightarrow x$ transition takes place for MgO above $v/v_0 = 0.751$, [5];
- the change in lattice parameter for SrS at $v/v_0 = 0.629$ is the same as for S

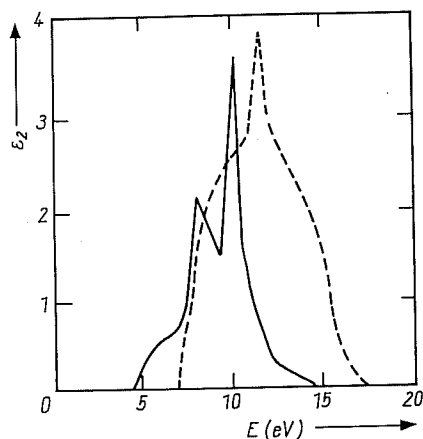


Fig. 3. Calculated dielectric function ($\epsilon_2(\omega)$) for MgO in normal pressure ($v/v_0 = 1$) (—) and under high pressure ($v/v_0 = 0.751$) (---)

substitution by O. The comparison of SrO and SrS under pressure is in progress now.

The band structures obtained are given in Fig. 2a and b. The (Γ , Δ , X) bands which are due to s-states of cation and anion under hydrostatic pressure increase related to Γ_{15} while a decrease of ($\Gamma_{25'}$,

Δ_2 , X_3) bands due to d-states of the cation is observed, too. Nevertheless, the difference between energies of the Γ_{15} and Γ_1 states is increasing more rapidly than the decrease of the difference between energies of states X_3 and X_5 . Consequently a faster change of s-states is seen under pressure than that of d-states. The conduction band under pressure is also changed. In the band ($\Gamma_{25'}$, Δ_2 , X_3) a transition of d-states of the cation into d-states of the anion is observed, while in the band (Γ , Δ , X) a part of cation s-states and the anion s-states goes over into d-states. A similar s-d transition was observed also before /10/.

The $\epsilon_2(\omega)$ of MgO calculated in normal state and under pressure is shown in Fig. 3. We can observe that the application of a pressure led to a shift towards the range of high energies concerning the absorption edge and smearing of the first peak as well as to some general increase in intensity.

The shift of the absorption edge can be explained by the raising of the Γ_1 state in the conduction band (the absorption edge is caused by the $\Gamma_{15} \rightarrow \Gamma_1$ transition). At the same time, the X_3 state is sinking in the conduction band and a slower sinking of X_5' in the valence band is observed. For increase of pressure the absorption edge will be due to the $X_5' \rightarrow X_3$ transition and will shift toward the range of smaller energies (the $\Gamma_{15} \rightarrow X_3$ transition was not considered by us, since we supposed that the probability of the indirect transition is small compared to the direct transition).

Overlapping of the first peak with the second one causes a smearing of the peaks, which effects either to 'equalization' of conduction band and to increase of the valence band-width.

The square values of matrix elements as probabilities of the optical transition in high symmetry points of the Brillouin zone are shown in Table 1. An increase of

T a b l e 1

Comparison of squares of matrix elements of MgO
in characteristic optical transitions

transition	MgO $ e M_{c,v}(k) ^2$	
	normal pressure	high pressure
$\Gamma_{15} \rightarrow \Gamma_1$	0.19	0.29
$X_{5'} \rightarrow X_3$	0.17	0.30
$L_3 \rightarrow L_{2'}$	0.19	0.29
$W_1 \rightarrow W_3$	0.05	0.06

the values of matrix elements is observed under hydrostatic pressure. This explains partly the increase of the spectrum intensity.

References

- /1/ V.S. STEPANYUK, A. SZASZ, and A.A. KATSNELSON, phys. stat. sol. (b) 155, 215 (1989).
- /2/ V.S. STEPANYUK, A.A. GRIGORENKO, and A.V. KOZLOV, Fiz. tverd. Tela 31, 58 (1989).
- /3/ E.V. STEPANOVA, V.S. STEPANYUK, and M.N. ROGALEVA, Fiz. tverd. Tela 30, 2303 (1988).
- /4/ P. HOHENBERG and W. KOHN, Phys. Rev. 136, 864 (1964).
- /5/ K.J. CHANG and M.L. COHEN, Phys. Rev. B 30, 4774 (1984).
- /6/ S.K. DE and S. CHATTERJEE, Phys. Rev. B 40, 12304 (1989).
- /7/ D.D. KOELING and G.O. ARBMAN, J. Phys. F 5, 2041 (1975).
- /8/ G. LEHMAN and M. TAUT, phys. stat. sol. (b) 54, 469 (1972).
- /9/ F. BASSANI and G. PASTORI-PARRAVICINI, Electronic States and Optical Transitions in Solids, Pergamon Press, Oxford 1975 (p. 260).
- /10/ L. YUSSOUFF (Ed.), Electronic Band Structure and Its Applications, Proc. Internat. School at the Indian Institute of Technology, Kanpur 1986.

(Received March 27, 1992)