phys. stat. sol. (b) **155**, 179 (1989)

Subject classification: 71.25; 78.20; S10.1

Department of Solid State Physics, Lomonosov State University, Moscow[1]) *(a), Laboratory of Surface and Interface Physics, Eötvös University, Budapest*[2]) *(b), and Department of Solid State Physics, Voronezh State University*[3]) *(c)*

Electronic Structure and Optical Properties of MgO

Band Structure Calculation and Cluster Model

By

V. S. STEPANYUK (a), A. SZÁSZ (b), B. L. GRIGORENKO (a), O. V. FARBEROVICH (c), and A. A. KATSNELSON (c)

The electronic structure of MgO is calculated in the framework of local-density theory using the LAPW resp. cluster X_α-SW method. The results of an improved permittivity calculation is compared with optical measurements, yielding good agreement. The effect of pressure on the electronic structure is studied for NaCl symmetry. It is found that the direct gap becomes indirect already for a compression of $V/V_0 = 0.9$.

Die Elekronenstruktur von MgO wird im Rahmen der lokalen Dichtefunktionaltheorie mit LAPW, bzw. mit der Cluster-X_α-SW-Methode berechnet. Die Ergebnisse einer verbesserten dielektrischen Permittivitätsbestimmung werden mit den experimentellen optischen Daten verglichen und ergeben gute Übereinstimmung. Die Druckabhängigkeit der Elektronenstruktur wird für NaCl-Symmetrie untersucht und gefunden, daß die direkte Bandlücke schon für eine Kompression von $V/V_0 = 0{,}9$ indirekt wird.

1. Introduction

Recently increasing scientific interest has been turned toward the metal–oxygen systems. The wide scale of their physical and chemical properties, as thermostability, resistivity against the chemical corrosion, as well as some wide range properties useful for optical elements are the cause of their scientific interest. The difficulties of the interpretation of their electronic energy band structures and their pressure-induced variation as well as the explanation of the measured optical spectra promoted a number of theoretical investigations as well. In our present paper we describe a calculation of electron-energy spectra and optical properties of MgO (NaCl structure) trying to clarify some contradictions in the corresponding literature [1].

In Section 2 the electronic structure of MgO is calculated by the self-consistent linear augmented plane wave (LAPW) method [2]. In Section 3 we give a comparison of the theoretically approximated spectrum for the imaginary part of dielectric permittivity $(\varepsilon_2(\omega))$ with the experimentally measured data.

In Section 4 we describe the pressure-induced change of the electronic energy band spectra.

In Section 5 we choose an appropriate cluster calculation of MgO, and a comparison is given with the electronic structure calculated for bulk MgO.

---

[1]) Leninskie Gory, SU-117234 Moscow, USSR.
[2]) Muzeum krt. 6—8, H-1088 Budapest, Hungary.
[3]) SU-394693 Voronezh, USSR.

2. The Band Calculation

The electron-energy band structure of MgO was calculated by use of the self-consistent LAPW method [2] in the frame of the local approximation of density functional theory [3, 4]. The accuracy of our calculation is 0.013 eV.

In Fig. 1 the calculated self-consistent electronic structure is shown. It is characteristic that the lower valence band is formed by s-electrons, while the upper valence band is formed by electrons of oxygen. Moreover, it can be observed that the top of the valence band and the bottom of the conduction band are located at symmetry point Γ_1, consequently MgO is a direct-band dielectric. Some characteristic parameters of the MgO electron-band structure are listed in Table 1. Considering the problems of the electronic density functional method [4], the value of the band gap is underestimated.

3. Optical Spectrum

The calculation of the imaginary part of the dielectric permittivity $(\varepsilon_2(\omega))$ generally has been carried out in the approximation of constant matrix element. It became clear, that such a calculation is not entirely consequent [5]. For the correction of this problem in our recent paper $\varepsilon_2(\omega)$ is calculated taking into consideration the energy dependence of the matrix elements of optical transitions.

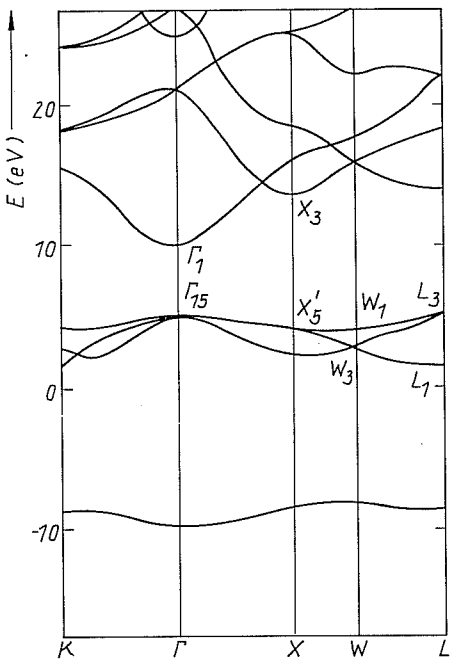

Fig. 1

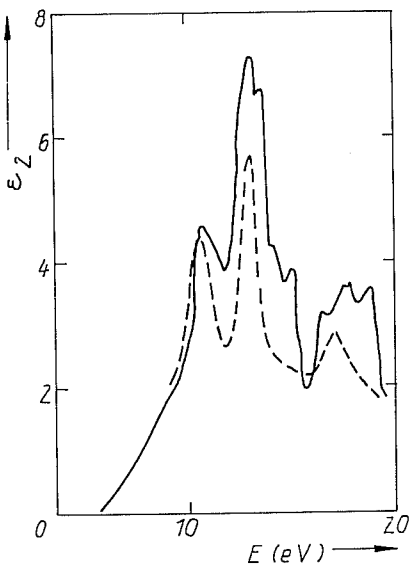

Fig. 2

Fig. 1. The calculated band structure of MgO

Fig. 2. The imaginary part of the dielectric permittivity of MgO. — — — experiment [1], ——— present theory

Table 1
The characteristic energies (in eV) of various symmetry points and comparison with experiments

Γ_1	Γ_{15}	Γ_1	X_3	L_1	L_3	W_3	W_1	E_g theor.	E_g exp. [12]	E_z (sp) theor.	E_z (sp) exp. [12]	E_z (p) theor.	E_z (p) exp. [12]
−11.053	5.976	10.958	14.659	1.351	5.331	2.998	4.272	4.982*)	7.77	17.029*)	21	4.525*)	5 to 6
								4.50 [12]		17.14 [12]		4.80 [12]	
								7.80 [13]		18.5 [13]		5.3 [13]	
								4.87 [14]		—		—	
								5.37 [15]		17.20 [15]		4.07 [15]	

*) Present calculation.
E_g energy band gap.
E_z(sp) width of sp-valence band.
E_z(p) width of p-valence band.

From these calculations [6] ε_2 was found

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

where

$$\varrho_{\mathrm{cv}}(\boldsymbol{k}) = \langle \boldsymbol{k}, \mathrm{c}| \, -i\nabla \, |\boldsymbol{k}, \mathrm{v}\rangle$$

and $\langle \boldsymbol{k}, \mathrm{c}|$, $|\boldsymbol{k}, \mathrm{v}\rangle$ are electron wave functions in conduction and valence band, respectively.

The recent calculation and the experimental spectrum [1] are compared in Fig. 2. The theoretical spectrum is shifted by an underestimated value of the band gap. For the correction of this effect an adjusting shift was made up to the correlation to Kohn-Sham eigenvalues [7 to 11]. The value of this shift is 2.9 eV. Under these circumstances the theoretical and experimental spectra agree well, so this adjustment should be considered as an accurate energy gap correction to the result of the electronic density functional method.

4. The Electronic Structure at High Pressures

A hydrostatic compression of the crystal was modeled by a 10% volume reduction. This means that the equilibrium lattice parameter ($a_0 \approx 0.4211$ nm) will change to $a = 0.4065$ nm ($V/V_0 = 0.9$), which can be considered much less than 10^{12} Pa, which approximates a higher volume ratio, $V/V_0 = 0.75$ [12]. The study of the real dependence of V/V_0 on pressure is in progress now. The energy band structure of MgO at this pressure is shown in Fig. 3. The valence band after the perturbation by pressure is practically unchanged compared to the valence band of MgO at normal pressure; but its band gap width has been lowered.

According to our recent calculation the hydrostatic pressure will lower the electronic energy in the vicinity of the symmetry point X_3 (d-states of Mg) in the conduction

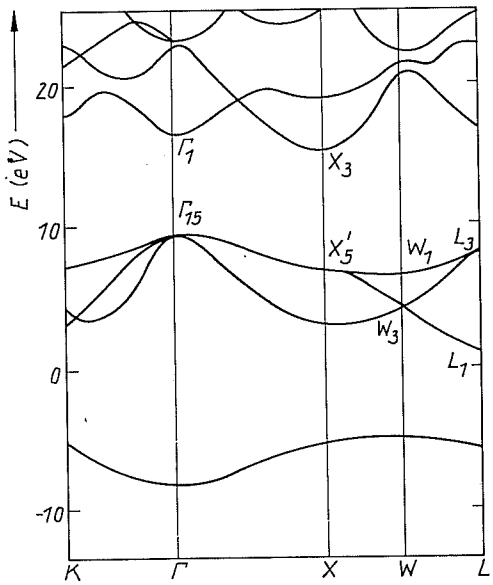

Fig. 3. The calculated band structure of MgO compound under homogeneous pressure

band, and a transformation of MgO into an indirect-band dielectric takes place. Our result is modifying the other calculations accepted in literature [12], where it was supposed that this transformation occurs only at considerably higher pressures, somewhere in the interval $0.5 \leqq V/V_0 \leqq 0.754$. Our result means that the transformation effect at about $V/V_0 = 0.9$ could be reached much easier in experiment.

5. Cluster Calculation

The electronic structure of MgO clusters was calculated by the X_α-SW method [16] as well.

The choice of the right size and geometrical arrangement of the cluster unit has essential importance. This problem could be solved by probing different parameters of the clusters. The optimal cluster can be chosen by comparison of the calculation results for a given cluster unit with the corresponding band-structure approximation.

The best result was obtained for the cluster size of 27 atoms (three coordination spheres) and obviously of NaCl structure symmetry.

The centre of this cluster is occupied by an Mg atom, the first coordination sphere consists of six oxygen atoms twelve Mg atoms are arranged in the second sphere, while the third sphere consists of eight oxygen atoms.

In Fig. 4 the electronic structure of this optimal cluster ($Mg_{13}O_{14}^{2-}$) is shown. The width of the band gap is equal to 5.03 eV, while the width of the valence band is 16.32 eV. The bottom of the valence band is mainly due to s-states of oxygen, the top of the band is formed by its p-states. It is clear from the above results that band calculation and the cluster calculation for the $Mg_{13}O_{14}^{2-}$ arrangement give similar patterns for the electron structure of MgO. It means that the cluster size chosen is realistic.

The cluster calculation is very important because of the possibility of using of the relatively simple cluster method instead of the more difficult band-structure calculation. The further work on these problems based on the chosen optimal cluster size is in progress.

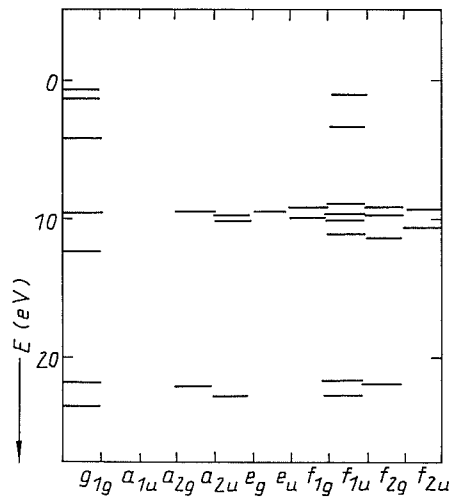

Fig. 4. The energy level diagram of the cluster $Mg_{13}O_{14}^{2-}$

6. Concluding Remarks

A calculation was carried out of electronic structure of MgO using both cluster and electronic band methods. The results obtained by the two calculations showed that the lower valence band is formed by s-states of oxygen, the other one is formed by p-states of oxygen, while the bottom of the conduction band is formed by s-states of Mg. Homogeneous pressure lowers the electronic energy of the X_3 point being basically created by d-electronic states of Mg. This change transforms the compound MgO into an indirect-band dielectric. The calculated spectrum of ε_2 is in good agreement with experiments.

Acknowledgement

The authors would like to thank Dr. S. F. Ryzankin for a program of cluster calculation by the X_α-SW method.

References

[1] V. B. Lazarev, V. V. Sobolev, and I. S. Shaplgin, Chemical and Physical Properties of Simple Metallic Oxides, Nauka, Moscow 1983 (in Russian).
[2] D. D. Koeling and G. O. Arbman, J. Phys. F **5**, 2041 (1975).
[3] P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964).
[4] S. Lundqvist and N. H. March, Theory of the Inhomogeneous Electron Gas, Plenum Press, New York/London 1983.
[5] V. S. Grigorenko, E. V. Stepanova, V. S. Stepanyuk, and A. A. Katsnelson, Vestnik Moskovskogo Univ. **30**, 3 (1989).
[6] F. Bassani and G. Pastori Parravicini, Electronic States and Optical Transition in Solids, Pergamon Press, Oxford 1975 (p. 260).
[7] M. S. Hybersten and S. G. Lonie, Phys. Rev. B **34**, 5390 (1986).
[8] P. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. Letters **56**, 2415 (1986).
[9] P. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. B **35**, 4170 (1987).
[10] P. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. B **36**, 6497 (1987).
[11] M. Aloni, L. Brey, and N. E. Christensen, Phys. Rev. B **37**, 1167 (1988).
[12] K. J. Chang, K. J. Marvin, and L. Cohen, Phys. Rev. B **30**, 4774 (1984).
[13] E. V. Zarochentsev, E. P. Proitskaya, and E. Y. Fain, Fiz. tverd. Tela **21**, 438 (1979).
[14] C. Y. Fonf, W. Saslow, and M. L. Cohen, Phys. Rev. **168**, 992 (1968).
[15] M. S. P. Bukovinsko, J. geophys. Res. **85**, 285 (1980).
[16] K. H. Johnson, Adv. Quantum Chem. **7**, 143 (1973).

(Received November 23, 1988; in revised form April 27, 1989)