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Electronic and structural properties of alkaline-earth oxides under high pressure

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The linear muffin-tin-orbital method in its tight-binding representation is used to calculate the band structures and to investigate the structural phase stability of MgO, CaO, and SrO under high pressures. The calculated equilibrium properties agree well with the experimental data. In CaO and SrO, the $B1$-$B2$ transition occurs at 557 and 317 kbar, respectively, which are in agreement with the experimental observations. For MgO the transition from the $B1$ to $B2$ phase is found to occur at a very high pressure of 1975 kbar. The electronic band structures at normal and at high pressures and the variation of fundamental band gaps as a function of pressure are calculated.

I. INTRODUCTION

The high-pressure behavior of the alkaline-earth oxides MeO (Me =Mg, Ca, Sr, Ba) has been studied extensively both experimentally and theoretically. This is because of their wide range of applications ranging from catalysis to microelectronics and their importance as prototype oxides. These are also used in refractory ceramics. Recently the study of the properties of these oxides has brought the attention of many workers, since these oxides are important constituents of earth's lower mantle where pressure reaches up to 1400 kbar. The electronic structure of these compounds inside the earth will be considerably changed compared to that at normal pressure. So they are of geophysical interest. At normal conditions these compounds crystallize in the NaCl-type structure and have both properties of ordinary insulators with wide band gap (E_g =7 to 10 eV) and properties of semiconductors with large valence bandwidth ($E_v > 6$ eV). Particular interest in these compounds is the NaCl-type ($B1$) to CsCl-type ($B2$) structural transformation which they exhibit under pressure.

For MgO no transition from the $B1$ to $B2$ phase has been observed experimentally for pressure up to 1200 kbar.[1,2] However a number of theoretical calculations were made for MgO. Diamond-anvil cell and shock-wave measurements show that CaO transforms from $B1$ to $B2$ phase over a pressure range of 600 and 700 (Refs. 3 and 4) kbar and SrO at 360 kbar.[5]

In this paper we present the results of the calculations of the band structures and structural properties for MgO, CaO, and SrO both in $B1$ and $B2$ structures. The linear muffin-tin-orbital method in its tight-binding representation[6] is used.

II. METHOD OF CALCULATION

The tight-binding linear muffin-tin-orbital (TBLMTO) method within the atomic-sphere approximation is used to obtain the electronic band structures. The details of the calculations can be found elsewhere.[7,8] The valence states for each of the compound namely Mg: 3*s* 3*p* 3*d*, Ca: 4*s* 3*p* 3*d*, Sr: 5*s* 4*p* 4*d*, and O: 2*s* 2*p* 2*d* were used. The core volume for the Mg 2*p* state is less than $0.25V_0$, where V_0 is the volume of the compound at ambient conditions. The problem of core-core overlap does not occur even in the high-pressure range (2000 kbar) considered here. Hence in MgO, the Mg 2*p* state is treated as frozen-core state. In CaO and SrO the hybridization of the semicore Ca 3*p* states and Sr 4*p* states with states on the other atoms cannot be neglected. The effect is more in Sr than in Ca, so it becomes necessary to treat the core *p* bands as relaxed valence-band states for CaO and SrO.

III. HIGH-PRESSURE PHASE TRANSITIONS

The calculated total-energy variations as a function of volume for each of the compound in both $B1$ and $B2$ structures are shown in Fig. 1. At ambient conditions all the three compounds are stable in the $B1$ structure. The calculated total energies were fitted to the Birch-Murunaghan equation of state to obtain the pressure-volume relation. The calculated equation of state for MgO, CaO, and SrO along with the experimental data points are shown in Fig. 2. The results for the equilibrium properties obtained from the polynomial fit are summarized in Table I and are compared with experimental and other theoretical work. The equilibrium lattice constant for MgO agrees very well with the experimental value. For CaO and SrO it is 2% less than the experimental value. The reason for this error is due to treating the semicore Ca 3*p* states and the Sr 4*p* states as relaxed band states.

The transition pressures are calculated at which the enthalpy of phase I becomes equal to that of phase II. The calculated pressure for the $B1$-$B2$ transition in MgO is 1975 kbar, which is accompanied by a volume reduction of 5.4%. This is lower than the value predicted by the pseudopotential[14] and the linear-augmented plane-wave method (LAPW).[13] However it is in agreement with the values predicted by the symmetrized-augmented plane-wave[16] and potential-induced breathing[12] (PIB) model. These results clearly show that there is no possibility for a $B1$-$B2$ transition in MgO even in the deep region of the earth's core mantle. For CaO and SrO the transition is found to occur at 557 and 317 kbar, respectively. The phase transitions are associated with a volume collapse of 10.7% for CaO and 11.4% for SrO.

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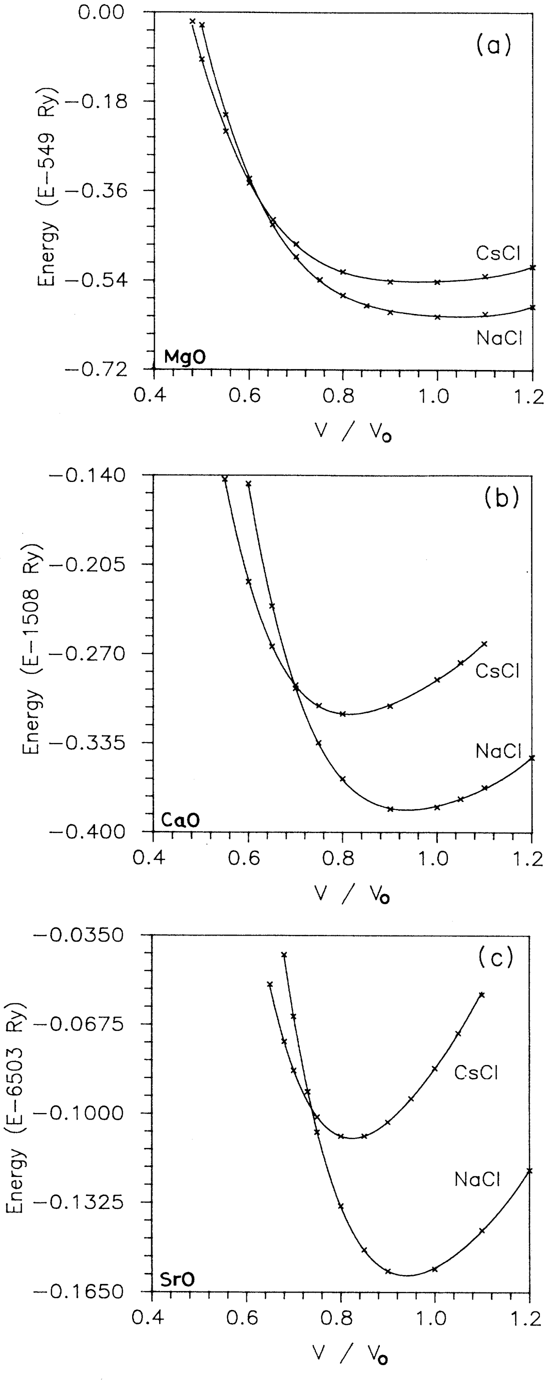

FIG. 1. Energy versus reduced volume for (a) MgO, (b) CaO, and (c) SrO.

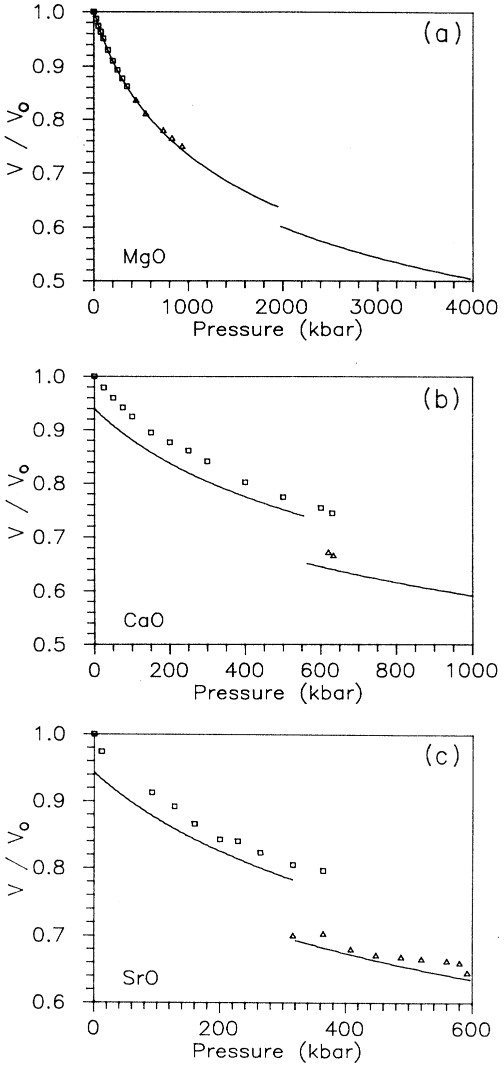

FIG. 2. (a) The calculated equation of state for MgO. The experimental data are from Ref. 9 (squares) and Ref. 2 (triangles). (b) The calculated equation of state for CaO. The experimental data are from Ref. 4 (squares and triangles). (c) The calculated equation of state for SrO. The experimental data are from Ref. 5 (squares and triangles).

This is in agreement with values reported in the literature. Even though the calculated values of transition pressures are slightly less than the experimental values, there is good agreement with other theoretical results.

IV. BAND STRUCTURES

The self-consistent scalar relativistic band structures for all three compounds were obtained in both $B1$ and $B2$ structures. The overall band profile is found to be in agreement with earlier works.[13,14,17,18] In MgO, the lowest-lying conduction band is mainly of Mg $3s$ type and the top of the valence band is purely of O $2p$ type. Since the s bands have their minima at Γ point and the p bands their maxima at Γ point, the compound will be an insulator with a direct gap at Γ. On compression the width of the valence-band increases. The direct band gap also increases. This is because the lowest energy point in the conduction band (Γ_1) moves away from the valence band. With further increase in pressure, more and more Mg $3d$ bands become filled which hybridizes with the $3s$ states. Now the low-lying conduction states have their minimum at the X point with the band gap between Γ and X point. This indirect band gap decreases on compression which

TABLE I. Equilibrium lattice constants and $B1$-$B2$ transition parameters for MgO, CaO, and SrO.

	MgO						CaO				SrO		
	Expt.	Present	PIBM[d]	LAPW[e]	Pseudo[f]	LCAO-HF[g]	Expt.[h]	Present	PIBM	LAPW	Expt.[i]	Present	PIBM
$a(B1)$ (Å)	4.21[a]	4.213	4.300	4.167	4.191	4.201	4.81	4.711	4.820	4.714	5.16	5.06	5.13
$V1(B1)/V_0$		0.636	0.605	0.495	0.377	0.629	0.744	0.738	0.747	0.784	0.815	0.782	0.779
$V2(B2)/V_0$		0.602	0.580	0.472	0.359	0.560	0.672	0.659	0.689	0.696	0.714	0.693	0.717
$V\%$		5.4	4.3	4.7	4.8	10.9	10	10.7	7.7	11.2	13	11.4	7.9
P_t (kbar)	>1000[b]	1975 ± 7	2510	5150	10 500	2200	630	557 ± 2	550	542	360	317 ± 2	360
B (kbar)	1620[c]	1676		1720	1 460	1708	1150	1338		1290	913[h]	1098	
$a(B2)$ (Å)		2.604			2.628	2.593		2.837					
E (eV)		0.93 ± 0.03						0.96 ± 0.03				0.68 ± 0.03	

[a] Reference 10.
[b] Reference 1.
[c] Reference 11.
[d] Reference 12.
[e] Reference 13.
[f] Reference 14.
[g] Reference 15.
[h] References 3 and 4.
[i] Reference 5.

arises due to the broadening of the bands. In CaO and SrO the lowest-lying unoccupied atomic orbital for the free Ca and Sr atom is of $3d$ and $4d$ type, respectively, whereas that for free Mg atom is of $3p$ type. Hence the band structures for CaO and SrO can be expected to be quite different from that of MgO. In CaO the conduction bands are formed due to the Ca $4s$ and $3d$ states. In the free Ca atom the unoccupied $3d$ states are slightly above the occupied $4s$ states. In the solid these $3d$ and $4s$ states hybridize and produce low-lying conduction states with more d components in particular at the X point. The low-lying conduction bands from these hybrids have their minimum at the X point causing CaO to be an insulator with an indirect gap between Γ and X point. The nature of the band gap in SrO is similar to that of CaO, where the lowest unoccupied orbitals of Sr are also of d type.

In the $B2$ phase the overall band profiles are found to be same except that the band gap is indirect with the top of the valence p band occurring at M and the bottom of the conduction band at Γ. The value of the valence bandwidth in the $B2$ phase is larger than that in the $B1$ phase. This is due to the reason that the crystal-field strength at the oxygen site is stronger in $B2$ phase when compared to $B1$ phase. In the $B2$ phase the nearest-neighbor distance is larger. However this larger nearest-neighbor distance is more than compensated by the larger coordination number. Also the smaller second-nearest-neighbor distance in $B2$ structure causes a larger O-O overlap, which further contributes to the broadening of the valence band. The effect of compression is same as in the $B1$ phase. The variation of band gaps with pressure in both $B1$ and $B2$ structures are summarized in Table II.

The calculated fundamental band gaps and the valence band widths at zero pressure are listed in Table III and are compared with available experimental and theoretical values. For SrO and CaO the fundamental band gaps are not available for comparison. However the direct band gap occurring at Γ has been measured experimentally. For MgO in the $B1$ structure the fundamental band gap is underestimated by about 38%. This order of error is the same as that generally found for semiconductors using the local-density approximation (LDA). The width of the valence band (p band) is quite close to the experimentally measured value and the other calculated results. Even though the band gaps are underestimated, the decreasing trend in the band gap with increasing size of the metal atom is reproduced.

V. CONCLUSIONS

Band-structure calculations for three insulating oxides namely MgO, CaO, and SrO in the $B1$ and $B2$ structures

TABLE II. Variation of band gaps and valence bandwidths as a function of reduced volume in MgO, CaO, and SrO.

	MgO			CaO			SrO		
	V/V_0	E_g	$E_v(p)$	V/V_0	E_g	$E_v(p)$	V/V_0	E_g	$E_v(p)$
NaCl	1.0	4.8 (Γ-Γ)	5.2	1.0	3.7 (Γ-X)	2.9	1.0	3.2 (Γ-X)	2.6
	0.7	8.6 (Γ-X)	7.4	0.8	3.6 (Γ-X)	3.5	0.85	3.0 (X-X)	3.0
	0.55	8.0 (Γ-X)	9.2	0.7	3.3 (Γ-X)	3.9	0.75	2.4 (X-X)	3.6
CsCl	1.0	2.8 (M-Γ)	6.7	1.0	2.3 (M-Γ)	4.0	1.0	2.4 (M-Γ)	3.2
	0.7	5.6 (M-M)	9.4	0.7	2.2 (M-Γ)	5.1	0.7	2.3 (Γ-Γ)	4.1
	0.55	6.3 (M-M)	11.7	0.6	2.0 (M-Γ)	5.5	0.65	2.2 (Γ-Γ)	4.3

TABLE III. Energy band gaps and valence bandwidths in eV in the $B1$ structure.

	MgO						CaO				SrO			
	Expt.[a]	Present	Pseudo[c]	KKR[d]	LMTO[e]	*H-F*[f]	Expt.	Present	LMTO[i]	*H-F*	Expt.[j]	Present	LMTO[e]	*H-F*
$E_v(sp)$	21.0	17.7	17.1	17.2										
$E_v(p)$	5–6	5.2	4.8	4.1	4.4		3–4[g]	2.9	2.9			2.6	2.4	
Direct gap (Γ-Γ)	7.8[b]	4.8	4.5	5.4	6.1	8.2	7.0[h]	5.2	5.4	7.7	5.9	4.1	4.3	7.1
Indirect gap (Γ-X)								3.7	4.3	10.8		3.2	3.8	8.5

[a] Reference 19.
[b] Reference 20.
[c] Reference 14.
[d] Reference 21.
[e] Reference 17.
[f] Reference 22.
[g] Reference 23.
[h] Reference 24.
[i] Reference 18.
[j] Reference 25.

yield ground-state properties that are in good agreement with the experimental results and with the earlier calculations. The $B1$-$B2$ transition pressure for these compounds have been calculated and compared with experimental and other theoretical works. Our calculations are in reasonable agreement with the experimental results. The band gaps have been calculated as a function of pressure. Even in the compressed condition, since the ionic character still remains in the bonding, all the three oxides are found to be insulating near the transition pressure. In MgO, the band gap at $0.55V_0$ is 6.3 eV which is large, hence we cannot expect transition to metallic state. In CaO the band gap at $0.6V_0$ is 2.0 eV and in SrO it is 2.2 eV at $0.65V_0$. In these two compounds there is a possibility for band overlap metallization at further high pressures. The band-gap values at ambient conditions are underestimated by about 30–40 %. This error arises because of using LDA to the exchange-correlation potential. Even though LDA underestimates band gap, it is able to give correct ground-state and structural properties of these ionic crystals in which there is a rapid variation of charge density.

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