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Bonding and equation of state for MgO

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The bonding charge density in MgO is analyzed by the fitting of Slater-orbital expressions to the muffin-tin charge density derived in a self-consistent electronic-structure calculation. The ion densities that result suggest that a fully ionic bonding model is appropriate. Pair potentials, derived with the use of the Gordon-Kim method, are employed in the quasiharmonic approximation to calculate an equation of state and other properties of MgO. The results are analyzed in the light of previous similar calculations for alkali halides.

I. INTRODUCTION

The number of electrons transferred from one atom to another in forming a bond is a measure of the ionicity of the bond. Theoretical approaches which do not account for the change in crystal charge density as a function of ion displacement lead to ambiguities in the definition of this quantity. However, it has been shown that if the displacement of the ions is considered, a unique construction of a pseudoatom (ion) charge density exists.[1-3] Thus, in principle, a unique definition of ionicity can be achieved by merely integrating the pseudoion densities to determine how much charge is transferred from one atom to the other. In practice this would require a knowledge of the charge density of the system to first order in the displacements of the nuclei: this, of course, is not easily achieved. Nevertheless, it is important to understand that ionicity acquires a precise meaning in the framework of pseudoatom theory.

Recently Muhlhausen and Gordon[4] obtained quite accurate results for static properties of a large number of ionically bonded materials, including oxides, from calculations based on density-functional theory together with the assumption of full ionicity. In these calculations spherically symmetric charge densities for the ions in the crystalline environment were derived using a technique similar to that of Watson.[5] The quality of their results suggest that these fully ionic densities constitute reasonably accurate approximations to the true pseudoion densities. This conclusion is further supported by the work of Redinger and Schwarz,[6] who find a favorable comparison of overlapped Watson densities with the crystal density obtained from augmented-plane-wave (APW) calculations.

In this paper (Sec. II) a method for approximating the pseudoion charge densities for MgO is employed which, in principle, should be more accurate than the Watson sphere model. The pseudoion charge density is expressed in terms of Slater orbitals (SO) with the SO parameters derived by fitting to a "known" crystal charge density. (For this work the self-consistent muffin-tin charge density of Klein *et al.*[7] is used.) Ideally, the SO parameters should be determined by fitting the overlapped SO density to the known density everywhere in the unit cell. However, for MgO, satisfactory results were obtained by simply fitting the charge density of a single ion to the density inside its muffin tin.

The premise, which seems to be borne out by the results, is that by fitting realistic expressions (e.g., SO's) to the charge density inside the muffin tins, reliable estimates of the tails of these functions are extracted as well. The accuracy of the SO representation is demonstrated by the fit to the O $2s$ density: Only four SO terms are required to obtain four-place accuracy. When the charge densities of the resultant pseudoions are integrated to infinity their net charges turn out to be very near the fully ionic values.

Similarly derived pseudoion charge densities, with net charges constrained to be exactly the fully ionic values, are used (Sec. III) to calculate the equation of state. The method employed in the equation-of-state calculations follows that used previously in similar calculations for the alkali halides.[8] The essential difference is that the charge density of the alkali-halide crystal was taken to be the sum of free-ion densities, while the present results for MgO are based on an electronic-structure calculation for the solid, a refinement which is absolutely necessary for oxides since the free O^{2-} ion is unstable. The charge densities are used to calculate pair potentials using the Gordon-Kim[9] method. The pair potentials are then used in the quasiharmonic approximation to calculate the equation of state. Theoretical results for elastic constants, phonon frequencies, thermal expansion, and melting temperature are compared with experimental data.

II. CHARGE DENSITY

We want to approximate the pseudoion charge densities for magnesium and oxygen in MgO from the total charge density obtained in a self-consistent band-structure calculation in the muffin-tin approximation.[7] The energy levels of MgO form six separate filled bands corresponding to 1*s*, 2*s*, and 2*p* levels of Mg and O. The charge density of a Mg (O) band is assumed to be a sum of spherically symmetric densities located on the Mg (O) sites. For each band, an expression of the form

$$\rho(r)=\left[\sum_i \alpha_i r^{n_i} e^{-\beta_i r}\right]^2 , \tag{1}$$

is chosen to represent this spherically symmetric density. In Eq. (1) r is the distance from the nucleus, α_i and β_i are parameters to be determined by fitting to the known density in the appropriate muffin tin, and the n_i are integers (0 or 1 in our case). The fit is more easily obtained by working with the square root of Eq. (1). Specifically, the parameters α_i and β_i are selected to give the least-squared deviation of

$$S=\sum_j \left[\phi_0(r_j)-\sum_i \alpha_i r_j^{n_i} e^{-\beta_i r_j}\right] , \tag{2}$$

where $|\phi_0|$ is the square root of the known charge density (ρ_0) and the r_j are selected points in the muffin-tin sphere. The wave function of a 2*s* state has one node at a value of r which depends on its energy within the band. However, the nodes for different states within a band are near enough together they pose no real difficulty in fitting the total charge density of the band to a single orbital; the sign change in ϕ_0 being selected to coincide with the minimum in $\rho_0(r)$. This question does not arise for the 1*s* and 2*p* states since they have no nodes.

The charge density of the deep (low-energy) "bands" is, of course, localized almost entirely within the muffin-tin spheres. For these levels, Mg 1*s*, Mg 2*s*, Mg 2*p*, and O 1*s*, the exponential parameters (β_i) were taken from the tables of Clementi and Roctti.[10] For the O 2*s* and O 2*p* levels the β's as well as the α's were varied to give the best fit to the densities. Optimum values obtained for these parameters are listed in Table I. Following the notation in Ref. 10 the coefficients, C_i, are related to α_i by

$$\alpha_i=\left[\frac{Z_f(2\beta_i)^{2(n_i+3/2)}}{4\pi[2(n_i+1)]!}\right]^{1/2} C_i , \tag{3}$$

where $Z_f=2$ (6) for *s* (*p*) states. The parameters in the first six columns of Table I were obtained by minimizing S^2 with the added constraint, imposed by the Lagrange multiplier technique, that the integrated charge,

TABLE I. Slater-orbital parameters for the various energy levels in MgO obtained by fitting to the muffin-tin charge density.

	Mg 1*s*[a]	Mg 2*s*[a]	Mg 2*p*[a]	O 1*s*[a]	O 2*s*	O 2*p*	O 2*s*[b]	O 2*p*[c]
n	0	0	1	0	0	1	0	1
	0	0	1	0	0	1	0	1
	1	1	1	1	1	1	1	1
	1	1	1	1	1		1	
	1	1		1				
β	17.0027	17.0027	12.5886	13.8996	16.0207	7.744 42	16.0207	7.744 42
	11.4473	11.4473	6.050 91	7.681 81	6.395 15	3.249 18	6.395 15	3.249 18
	10.7043	10.7043	3.405 54	6.470 42	2.853 88	1.212 46	2.853 88	1.212 46
	4.974 55	4.974 55	2.446 51	3.142 95	1.409 17		1.409 17	
	3.307 79	3.307 79		1.886 06				
C	0.131 61	−0.018 93	0.010 15	0.052 94	−0.004 37	0.015 48	−0.004 40	0.015 83
	0.805 70	−0.231 26	0.309 28	0.886 09	−0.273 02	0.390 89	−0.272 91	0.388 50
	0.092 20	−0.095 54	0.461 68	0.108 06	0.621 75	0.721 99	0.620 43	0.729 59
	−0.028 90	0.410 67	0.292 95	−0.091 61	0.506 15		0.509 31	
	0.021 27	0.691 40		0.093 42				

[a] β's obtained from Ref. 10.

[b] Unconstrained total charge ($Z=2.01$).

[c] Unconstrained total charge ($Z=6.06$).

$$Z \equiv 4\pi \int_0^\infty r^2 \rho(r) dr , \tag{4}$$

equal Z_f exactly. As expected, for the localized states, Z and Z_f are nearly equal without the constraint. Somewhat surprisingly Z and Z_f were found to be about equal for the O 2s and O 2p states as well. The proximity of Z to Z_f ($Z = 2.01$ for O 2s and $Z = 6.06$ for O 2p) suggests that the bonding is fully ionic. The last two columns (Table I) give the SO parameters obtained with no constraint on Z. The values for β_i obtained in the unconstrained Z fit were then held fixed in the $Z = Z_f$ fit.

The quality of the fit for the O 2s density is shown in Table II. We see that four-place accuracy is attained with only four terms in Eq. (1). A similar quality fit was obtained for the O 2p density using three SO terms, the parameters for which are listed in the last column of Table I. The fact that highly accurate fits, with reasonable values for Z, are obtained with only a few parameters give some measure of confidence in the tails of these functions.

TABLE II. Four-term Slater-orbital fit to the O 2s muffin-tin charge density ($\phi^2 = \rho$).

r (bohr)	ϕ_0 (True value)	ϕ (Fitted value)	Deviation
0.0211	−3.1478	−3.1484	0.0006
0.0511	−2.4404	−2.4401	−0.0002
0.0955	−1.6295	−1.6293	−0.0001
0.1732	−0.6870	−0.6872	0.0002
0.3641	0.2831	0.2832	−0.0001
0.5239	0.4770	0.4769	0.0002
0.6216	0.4925	0.4918	0.0007
0.7104	0.4748	0.4748	−0.0000
0.7814	0.4503	0.4503	0.0000
0.8880	0.4054	0.4055	−0.0001
0.9590	0.3738	0.3739	−0.0002
1.0301	0.3426	0.3428	−0.0002
1.1011	0.3127	0.3129	−0.0002
1.1722	0.2846	0.2848	−0.0003
1.2787	0.2472	0.2465	0.0007
1.3853	0.2125	0.2128	−0.0003
1.4563	0.1926	0.1929	−0.0003
1.5984	0.1581	0.1585	−0.0004
1.7760	0.1246	0.1243	0.0003
1.9891	0.0936	0.0935	0.0001
2.1312	0.0775	0.0776	−0.0001

III. EQUATION OF STATE

The approximations used in the present calculations of the equation of state for MgO are discussed in Ref. 8 and briefly outlined below. First of all, it is assumed that the electrons stay in their ground state as the nuclei move (adiabatic approximation). Notwithstanding the higher temperatures considered here ($\sim$3000 K or 0.25 eV) this approximation is expected to remain valid for MgO because its band gap, $E_g \sim 8$ eV, is much larger than kT (corrections entering as $e^{-E_g/kT}$) and several orders of magnitude larger than typical phonon frequencies (corrections entering as $h\nu/E_g$). The Gordon-Kim method for calculating pair potentials employs two approximations: (1) the rigid-ion approximation, in which the charge density of an ion pair is taken to be the sum of the densities of the constituent ions, and (2) the electron-gas approximation, in which the energy density is related to the charge density as though it were locally a free-electron gas. Next, the total potential energy of the crystal is assumed to be the sum of all the pair potentials (pair-potential approximation). Once the pair potentials are determined, it is a straightforward matter to calculate the classical normal-mode frequencies $[\nu_i(V)]$ of the crystal at any volume (V) we choose. By simply doing the lattice-dynamics calculation for a sequence of selected volumes we obtain the volume dependence of the frequencies, which in turn, provides the mechanism for thermal expansion. The vibrational part of the free energy of the crystal with volume V is obtained by assuming (quasiharmonic approximation) that its vibrational energy levels are those of independent harmonic oscillators with frequencies $\nu_i(V)$. The sum of the vibrational free energy and the potential energy of the static crystal gives the total free energy. Differentiating these terms with respect to V defines vibrational and static pressures, P_v and P_s,

TABLE III. Values obtained for γ and ξ by fitting the exponential form, $\gamma e^{-\xi r}$, to calculated values of the short-range Coulomb (SRC), kinetic-energy (KE), exchange (ex), and correlation (corr) contributions to the indicated pair potentials in the range r_l to r_u. Results are in atomic units with energy in hartree.

Ion pair	γ,ξ	SRC	KE	ex	corr	r_l	r_u
Mg-O	γ	−3.4244	78.3726	−7.6821	−0.1692	3.8	4.5
Mg-O	ξ	1.6670	1.8062	1.5333	1.1763	3.8	4.5
O-O	γ	−147.496	81.6919	−8.8949	−0.2786	5.2	6.6
O-O	ξ	1.7485	1.4386	1.1426	0.8730	5.2	6.6

TABLE IV. Comparison of room-temperature quasiharmonic frequencies to experimental phonon frequencies at selected symmetry points of the Brillouin zone.

Wave vector		Frequencies (cm^{-1})			
Γ	calc	410	1100		
	expt[a]	400	730		
X	calc	350	490	500	840
	expt[a]	280	430	450	550
L	calc	290	370	670	870
	expt[a]	280	350	550	600

[a] Reference 11.

which together give the quasiharmonic equation of state

$$P(V,T)=P_s(V)-P_v(V,T) .$$

The frequencies $\nu_i(V)$ for a particular V determined by the quasiharmonic equation of state are referred to below as quasiharmonic frequencies. Finally, we neglect any effects due to thermally generated defects or surfaces.

The charge densities for Mg^{2+} and O^{2-} ions, expressed above in Table I, were used to calculate pair potentials, between Mg^{2+}-O^{2-}, Mg^{2+}-Mg^{2+}, and O^{2-}-O^{2-} pairs, using the Gordon-Kim method. Numerical values for the four contributions to the short-range part of these potentials [short-range Coulomb (SRC), kinetic energy (KE), exchange (ex), and correlation (corr)] were then used to obtain the parameters of an exponential fit to each contribution. The resultant potentials are listed in Table III. Short-range interactions beyond second neighbors (nearest O-O pairs) and between cations were found to be negligible.

Results obtained for the room-temperature quasiharmonic frequencies, at the Γ, X, and L points of the Brillouin zone are compared with experimental results in Table IV. We see the agreement is reasonably good, within $\lesssim 25\%$, except for the longitudinal-optic modes for which we see calculated values that are too large by $\sim 50\%$. Similar agreement ($\lesssim 40\%$) is obtained for the elastic constants (Table V).

TABLE V. Comparison of room-temperature calculated (quasiharmonic) and measured bulk modulus $[B=(C_{11}+2C_{12})/3]$ and shear elastic contains ($C_{11}-C_{12}$ and C_{44}) in units of 10^{12} dyn/cm^2.

	B	$C_{11}-C_{12}$	C_{44}
calc	2.29	2.18	1.86
expt[a]	1.55	2.01	1.55

[a] Reference 11.

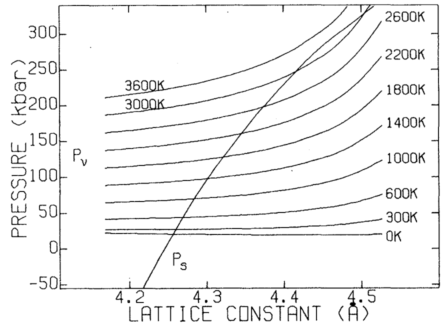

FIG. 1. Plot of the static pressure P_s and the vibrational pressure $P_v(T)$ (for selected temperatures), as a function of lattice constant.

The equation of state can be conveniently illustrated by plotting the static pressure (P_s) and the vibrational pressure $[P_v(T)]$ as a function of lattice constant a. The quasiharmonic equation of state obtained for MgO is plotted in this way in Fig. 1. [P_s (P_v) is positive (negative) for compression.] The value at a at temperature T is given by the intersection of P_s with $P_v(T)$. The calculated value of a at room temperature (4.260 Å) compares favorably with the experimental value (4.213 Å). For comparison, Cohen and Gordon[12] obtained 0-K values of 4.20 and 4.58 Å (experimental value of 4.203 Å) using, respectively, the charge densities of Yamashita and Asano[13] and Watson[5] in a modified electron-gas treatment. In similar calculations based on a self-consistent Watson-type density, with many-body

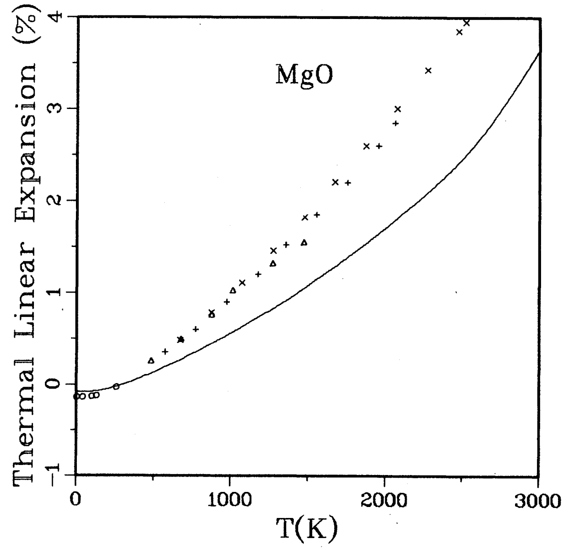

FIG. 2. Comparison of calculated thermal expansion of MgO (solid curve) with selected experimental data (○—Ref. 14, +—Ref. 15, ×—Ref. 16, and △—Ref. 17), as tabulated in Ref. 18.

corrections included, a value of 4.34 Å was obtained.[4]

Calculated and experimental results for thermal expansion are compared in Fig. 2. The results at low temperatures ($T < 1000$ K) are too low by ~40% while at high temperatures the discrepancy is reduced. This trend has been explained for the alkali halides as arising from inaccuracies due to the pair-potential assumption, which are partially cancelled at high temperatures by the neglect of anharmonic corrections. The error in the low-temperature thermal expansion for MgO is larger than that generally found for the alkali halides. This is to be expected because of the big difference between the size of the Mg^{2+} and O^{2-} ions (see argument in Ref. 8). However, another factor which could be important for MgO, is the neglect of any volume dependence in the pseudoion charge density. To include this effect would require self-consistent electronic-structure calculations for several lattice constants.

Finally, we note that the critical temperature $T_c = 3160$ K, above which the solid is unstable due to the $P_v(T)$ curves no longer intersecting P_s (see Fig. 1), and the melting temperature ($T_m \sim 3070$ K) are nearly equal. At T_c the isothermal bulk modulus, B_T, is zero. While the close agreement between T_c and T_m is partly due to the cancellation of errors discussed above, it nevertheless provides further evidence[8,19–23] that the $B_T = 0$ instability and melting are casually related.

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