

Band Structure Calculations of the High-Temperature Electronic Structure of Magnesium Oxide

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The effects of high temperature on the electronic structure of a material consist of two major contributions, thermal lattice expansion and the electron-phonon interaction. These can produce dramatic changes in the electronic structure and play a critical role in the high-temperature properties and behavior of ceramics. We have used *ab initio* pseudo-function band structure methods to calculate the temperature dependence of the electronic structure of MgO from 300 to 1300 K modeling the independent effects of thermal lattice expansion and the electron-phonon interaction. The band structure calculations were performed self-consistently on a (MgO)₄ supercell using experimental values obtained from high-temperature X-ray diffraction to determine the lattice constants up to 1300 K and the root mean square amplitude of phonon displacements. Lattice thermal expansion contributed -0.15 meV/K to the band gap temperature dependence. Individual phonon modes, with displacements in the $\langle 111 \rangle$, $\langle 110 \rangle$, and $\langle 100 \rangle$ directions, were modeled using distorted lattice calculations. The electron-phonon coupling was found to be strongest for the $\langle 100 \rangle$ mode modeled, with strong coupling seen for modes which lead to the smallest decrease in the Mg-O bond length. The overall magnitude of the electron-phonon contribution to the band gap temperature dependence for the phonon modes modeled was -0.95 meV/K. The theoretical results account for a band gap temperature dependence in MgO of -1.1 meV/K, which compares well with the temperature dependence of approximately -1 meV/K determined experimentally using vacuum ultraviolet spectroscopy. [Key words: band structure, electronic structure, magnesia, lattice, thermal properties.]

I. Introduction

THE high-temperature electronic structure of ceramic materials is important for determining the intrinsic properties at temperature, and as the framework in which extrinsic high-temperature properties such as dopant-induced electronic conductivity are to be understood. We desire to understand the high-temperature electronic structure of MgO so as to predict, from first principles and direct spectroscopic determination, the high-temperature electronic carrier concentrations and conductivity. We have carried out work of this sort for Al₂O₃,¹⁻³ but the simpler cubic structure of MgO permits a more detailed theoretical study of the major contributions to the temperature dependence of the electronic structure,

the thermal lattice expansion and electron-phonon interaction. A fundamental understanding of the effects of these two mechanisms on the high-temperature properties can also be used to understand the effects of stress and strain which are analogous to lattice dilatation, and defect density where the scattering by defects is comparable to the effects of thermally induced electron-phonon scattering.

Detailed theoretical descriptions of the temperature dependence of the electronic structure have been developed for the covalent semiconductors Si, Ge, and GaAs.⁴⁻⁸ The temperature dependence of the band gap is found to be flat (on the order of 0 meV/K) near $T = 0$ K, while the band gap decreases linearly from 200 K to several hundred K. In this linear region, the temperature coefficients observed for the covalent materials are much smaller (-0.22 meV/K for Si and -0.44 meV/K for Ge) than the temperature coefficients of 1.1 or 1 meV/K observed for α -Al₂O₃ and MgO, respectively. The band gap temperature dependence of ionic ceramics is comparable to that observed for ionic crystals such as the alkali halide KI (-0.85 meV/K,⁹ 1.05 meV/K¹⁰). The ionic nature of these materials is associated with a large degree of electronic charge localization in real space (as demonstrated by polaron formation) compared to the delocalized carriers and free-electron-like bands in covalent semiconductors.

It has been found for the covalent semiconductors that the temperature dependence of the electronic structure can be understood by modeling the effects of thermal lattice expansion and the electron-phonon interaction. The effects of thermal expansion on the electronic structure are usually determined from hydrostatic compression measurements, where the pressure coefficients or deformation potentials of the bands are determined. The electron-phonon interaction has previously been modeled as consisting of a Debye-Waller term and a self-energy term, utilizing a perturbation theory approach. The effects of the complete phonon structure, a complete set of all lattice vibrations, are introduced into the band structure calculation by using a broadened atomic potential to represent the time-averaged effect of all of the different atomic displacements. The use of the local pseudo-potential method for calculating the band structure is critical to successful implementation of this Debye-Waller approach to the electron-phonon interaction. For example, the Debye-Waller contribution would consist of multiplying the pseudo-potential Fourier coefficients $V(\mathbf{G})$ by $\exp[-(|\mathbf{G}|^2 \langle \mathbf{u}^2 \rangle / \mathbf{G})]$ where $\langle \mathbf{u}^2 \rangle$ is the mean square thermal vibration amplitude and \mathbf{G} is the reciprocal lattice vector in \mathbf{k} space. For MgO and other ionic oxides, a pseudopotential approach to the band structure calculation would be rather difficult to apply as the O pseudo-potential would be very deep, requiring many Fourier coefficients, and for the perturbation approach of the Debye-Waller formalism, it would be difficult to truncate these Fourier coefficients to zero easily.

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We have taken a new approach to computing the temperature dependence of the electronic structure for ceramics using the pseudofunction band structure method. The effects of thermal lattice expansion are calculated using the changes in the crystal structure determined from high-temperature X-ray or neutron diffraction studies. As temperature increases, thermal lattice expansion gives rise to dilatation of the unit cell, and it is this dilated unit cell which is used for the band structure calculation. The effects of the electron-phonon interaction are then modeled, in a unit cell with high-temperature cell parameters, by introducing the specific atomic displacements of a phonon vibration into the unit cell in real space. The band structure calculation is then performed on this distorted unit cell, allowing us to model a variety of electron-phonon modes considering the effects of different phonon modes, displacement directions and magnitudes to determine individual electron-phonon couplings. A manifold of these distorted cell calculations, for different phonon modes, can then be used to represent the behavior of the material at high temperature and to determine the magnitude of the electron-phonon interaction to be expected at high temperatures. In the present work, we have not used normal mode phonons, but have constructed arbitrary complex phonon modes. In addition, the vibrational amplitudes for the phonons modeled are varied up to the experimentally determined magnitude of the Debye-Waller factors for the temperature of interest. In subsequent work on the electron-phonon interaction, we plan to extend this approach to more realistically consider the phonon modes in the calculations through the use of normal mode phonons, whose vibrational amplitudes are determined by a Debye model taking into consideration the particular energy of each phonon mode calculated.

II. Methods

Band structure calculations were performed using the pseudofunction method,¹¹⁻¹³ which is a first-principles, self-consistent method using density functional theory and the local density approximation (LDA). The pseudofunction (PSF) energy band method utilizes a set of localized basis functions as in the standard linear combination of atomic orbitals (LCAO) approach. The orbitals are formed from radial solutions of the spherical part of the total potential for all atom sites in the unit cell. These spherical potentials are called the muffin tin potentials. In the augmented plane wave (APW) method of Slater,^{14,15} the potential was represented by muffin tin potentials with a constant potential between the muffin tins. The radius of the muffin tins is called the muffin tin radius. The solutions of the Schrodinger equation for the spherical potentials are done for some trial energy ϵ and the solutions are not bound. The trial energy ϵ is usually taken to be an energy in the middle of the bands of interest near the Fermi energy. In the PSF method, the radial solutions, along with the energy derivative of the radial solutions, are connected to spherical Neuman functions at a distance beyond the muffin tin radius. The Neuman functions have the correct behavior for tails of wave functions and their analytical form is convenient for doing some of the integrals in the Hamiltonian solution of Schrodinger's equation. Some features of the energy bands, such as the band gap, can be quite sensitive to the choice of the energy parameter ϵ . For simple systems, ϵ can be optimized by computing the minimum total energy of the complete system. The calculations reported here are too complex to permit optimizing ϵ . Instead, we have found, through the use of two different basis sets for the calculations, that the results for the temperature dependence are not sensitive to the choice of ϵ , even though the one-electron energies vary with the choice of basis set. Thus, we will show that the results are not sensitive to ϵ . This problem of choosing ϵ is common to all methods that use a linearized basis set such as the linear muffin tin orbital (LMTO)¹⁶ and LAPW

methods. It is not usually mentioned as there is a standard way to choose it: in the middle of bands near the Fermi energy.

The PSF method, in addition to most current one-electron band structure methods, utilizes the local density approximation and, therefore, is found to underestimate the band gap energy because of the additional effects of many-body interactions. It is thought that the conduction bands are reasonably represented under the local density approximation while the bands can simply be shifted to obtain the experimental band gap energy. Previous PSF calculations of the room-temperature band structure of MgO performed using a face-centered cubic MgO unit cell have shown very close agreement between the calculated band energies and those derived from semianalytic critical point fitting of vacuum ultraviolet optical data, disregarding the underestimate of the minimum band gap energy.¹⁷ Many-body corrections to the LDA are only now being studied, but it appears that the corrections are only a small function of interatomic spacing.¹⁸ We therefore feel that the band gap changes calculated assuming the LDA can be used directly to represent the true band gap temperature dependences arising from either lattice expansion or the electron-phonon interaction. The many-body corrections would only add a constant to all of the band gaps calculated.

The basis set used for the band structure calculations consists of sp^3d^5 orbitals on the Mg site and sp^3 orbitals on the O site. ϵ on the O site was always chosen to be in the middle of the filled O p bands as is the common practice. ϵ for the Mg radial solutions was chosen to be at the top of the filled O states for the first case and at the bottom of the empty Mg states for the second case. The band structure was not sensitive to this choice of ϵ , even though the band gap shifts significantly. Two different, nonorthonormal basis sets were used. Basis set 1 gave a band gap of 3.73 eV and was used for the lattice expansion calculations at three temperatures: 300, 973, and 1300 K. Basis set 2 gave a band gap of 5.39 eV and was used for lattice expansion calculations at 300 and 1300 K, and also for the 10 electron-phonon calculations.

The calculations reported here were performed on an (MgO)₄ supercell, to allow the modeling of individual phonon modes with greater complexity and lower symmetry than can be represented in the fundamental MgO unit cell. The supercell used for the present calculations leads to very similar band structures at room temperature as compared to a band structure calculated for the fundamental unit cell. One difference arises because the Brillouin zone reciprocal lattice vectors of the supercell are shorter in k space than for the fundamental unit cell, since the real space supercell vectors are longer than the fundamental unit cell dimensions. This leads to a folding in of the bands in k space for the supercell calculations. The band structures reported here are labeled using the fcc fundamental Brillouin zone critical point scheme.¹⁹

The effect of thermal lattice expansion is modeled in a series of band structure calculations where the lattice constant increases as determined from the X-ray and neutron data. The electron-phonon interaction cannot be modeled exactly since we lack knowledge of the spectrum of phonons, or phonon structure, as a function of temperature. We therefore model the electron-phonon interaction for explicit phonon vibrations by displacing the Mg and O atoms to determine what sorts of atomic displacements can give the experimentally observed changes in the band gap energy. Any arbitrary atomic displacements that we choose can be expressed as a linear combination of phonon normal modes. We have not decomposed our phonons into the normal phonon modes, instead choosing to highlight the relative importance of motions that conserve nearest-neighbor bond lengths as compared to motions that significantly change bond lengths. These calculations are too costly to attempt a huge number of configurations to represent all of the possible phonon modes. It is also impractical to optimize the basis sets so that total energies can be computed for each configuration. We will simply compute

how the energy bands change with particular displacements. In a real crystal, all phonon modes are excited but with unknown densities or occupation numbers, which probably depend sensitively on the total energy. The density of phonons in a particular mode, or the occupation number of that mode, will determine the magnitude of the atomic displacements for that mode at a certain temperature. We have not attempted to determine the occupation-determined magnitude of displacements for each mode that we model, instead using the mean square thermal displacements as an upper limit for displacements of any modes modeled. We should add that we did find that the total energy favors distortions that do not alter the Mg–O bonds as compared to modes that greatly alter the Mg–O bond length, suggesting that these bond-length-conserving modes are of low energy and can be expected to be highly occupied.

The high-temperature atomic structure of MgO has been determined by Hazen,²⁰ who reports both the thermal lattice expansion of the unit cell and the high-temperature Debye–Waller factors of Mg and O atoms. The Mg–O bond length at 296 K is 2.106 Å (1 Å = 0.1 nm) and expands to 2.132 Å at 1300 K, an expansion of 1.35%. The Debye–Waller factors were reported up to 900 K and vary linearly with temperature above room temperature. At room temperature, the Debye–Waller factor B ($B = 8\pi^2 u^2$ where u is the rms displacement in angstroms) for Mg and O atoms is 0.34 and 0.37 Å² corresponding to vibrational amplitudes of 0.067 Å. We have linearly extrapolated the reported Debye–Waller factors to 1300 K, where $B = 2.02$ Å² and the rms magnitude of the atomic vibrations of both Mg and O is 0.16 Å. At room temperature, the phonon displacements in MgO are very small and do not play an important role in determining the band gap energy at room temperature. At high temperatures, the phonon displacements are very large and, in our calculations of the electron–phonon interaction at 1300 K, we have displaced the Mg and O atoms up to 0.16 Å.

Using vacuum ultraviolet spectroscopy,^{21,22} we have determined the band gap temperature dependence to be approximately 1 meV/K from room temperature to 1000 K.¹⁷ This is comparable to the results found for Al₂O₃,³ and is much larger than found for covalent semiconductors. In addition, using valence band X-ray photoemission techniques,³ we have found the upper O 2*p* valence bandwidth to be 6.7 eV.

III. Results and Discussion

The room-temperature band structure for MgO, using basis set 1, is shown in Fig. 1. The band gap is found to be direct at the Γ point. The valence bands are relatively flat in k space, demonstrating the localized nature of these electronic states. The lowest conduction band exhibits noticeable curvature in k space, representative of more delocalized electronic states, while the upper conduction bands are flatter, corresponding to greater localization of the electron wave functions in real space. The band effective masses of the electrons and holes are determined by the band curvature in k space and are of use for high-temperature electronic conductivity analysis. The band effective masses at Γ are $m_e^* = 0.14m_e$ for the conduction band and $m_h^* = 1.35m_e$ and $m_h^* = 0.17m_e$ for the heavy and light hole valence bands. The total density of states (DOS) and Mg and O partial DOS, determined by integrating the charge in the Mg and O muffin tin regions, are shown in Fig. 2 with the energy scale referenced to the top of the valence band. The O 2*s* lower valence band states are seen at -15 eV, while the upper valence band exhibits a two-peak character characteristic of most simple oxide ceramics. The lower peak of the upper valence band, at approximately -4 eV, arises from a mixture of charge on both the Mg and O sites and corresponds to Mg–O covalent bonding orbitals or states. The upper peak in the upper valence band at approximately -2 eV arises from charge on the oxygen sites and

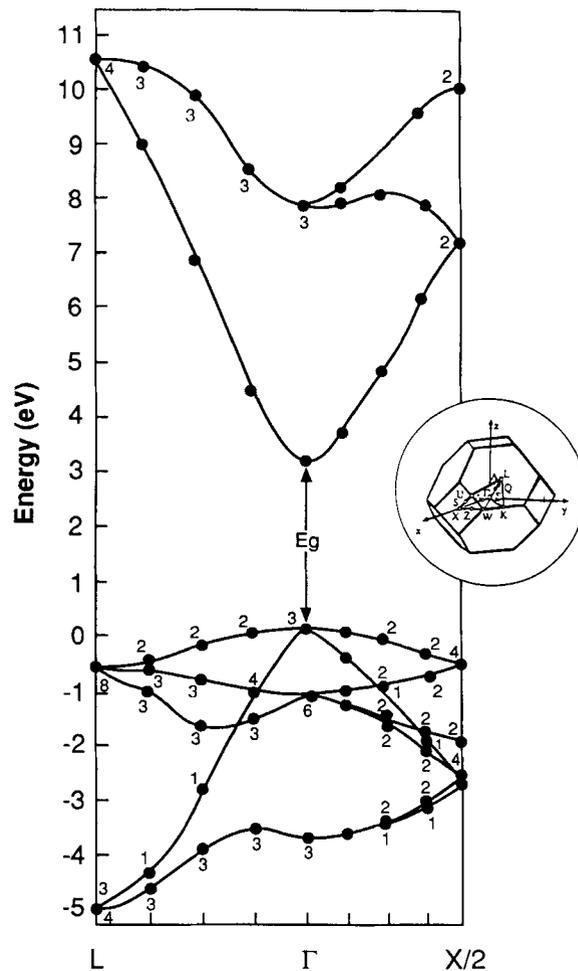


Fig. 1. Band structure calculated for (MgO)₄ at room temperature, using basis set 1; the numbers indicate the band degeneracies at different points in k space.

arises from O 2*p* nonbonding orbitals. The lowest conduction band peak, seen at approximately 5 eV in the calculated DOS because of the underestimate of the band gap energy, arises from Mg 3*s* antibonding states. At approximately 9 eV, the second peak in the conduction bands arises from Mg 3*p* states. The upper valence band DOS determined from the

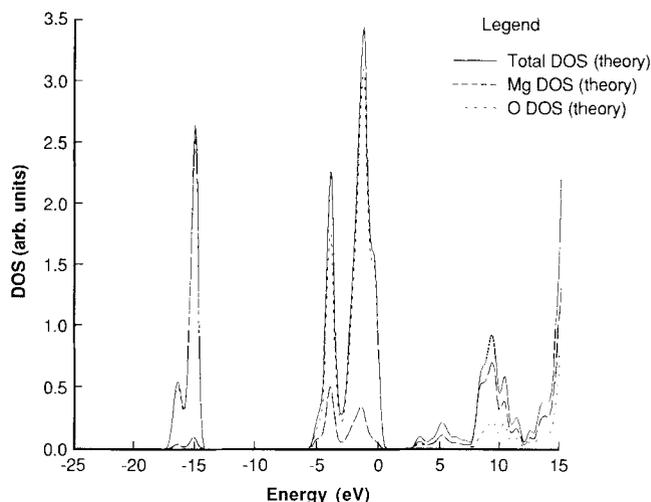


Fig. 2. Calculated total density of states and Mg and O partial density of states for (MgO)₄ at room temperature.

band structure calculation and experimentally using valence band X-ray photoemission spectroscopy (vb-XPS) is shown in Fig. 3. The upper valence bandwidth is seen to be 6 eV, with good agreement between theory and experiment, giving us confidence in the band structure calculations.

(1) Thermal Lattice Expansion

The contribution to the band gap temperature dependence arising from thermal lattice expansion was calculated directly by dilating the $(\text{MgO})_4$ supercell up to 1.35%, corresponding to the expansion from room temperature to 1300 K. The results of these three calculations for basis set 1 are shown in Fig. 4, where the effects of thermal lattice expansion give rise to a -0.15 eV change in the band gap energy. Similar calculations using basis set 2 also produced a -0.15 eV change in the band gap. Therefore, we find in MgO that -0.15 meV/K of the band gap temperature dependence arises from lattice expansion.

From these calculations, we are also able to theoretically determine the hydrostatic band gap strain coefficient or deformation potential for MgO, of use in surface stress determination.²³ The shift of the band gap or exciton peak under applied surface stresses can be used with the deformation potentials of the band gap to determine from first principles the surface layer stresses present. Pure lattice dilatation as used here to model thermal lattice expansion is comparable to bulk hydrostatic strain. The deformation potential that we determine for MgO is $dE_g/d(\text{lin.}\% \text{ strain}) = 120$ meV/(lin.% strain).

(2) Electron-Phonon Interaction

The electron-phonon interaction was modeled using distorted lattice calculations for individual phonon modes. We calculated the additional effect of the phonons on the high-temperature $(\text{MgO})_4$ unit cell. We initially studied phonons with the atoms displaced in $\langle 111 \rangle$ directions, with the direction cosines randomly selected. The results of these calculations are shown in Fig. 5. The different phonon modes studied are summarized in Fig. 6. In the four calculations labeled A, the oxygen atoms were left in their equilibrium positions while the Mg atoms were displaced 0.16 Å. Calculations labeled B and C had both the Mg and O atoms displaced 0.08 and 0.16 Å. None of these calculations produced dramatic band gap decreases; the electron-phonon coupling for these modes is small. This may be due to the fact that these modes all lead to pronounced decreases in the Mg-O bond lengths from 2.13 Å with no phonon to as low as 1.94 Å.

We therefore created $\langle 100 \rangle$ (D) and $\langle 110 \rangle$ (E) modes with spe-

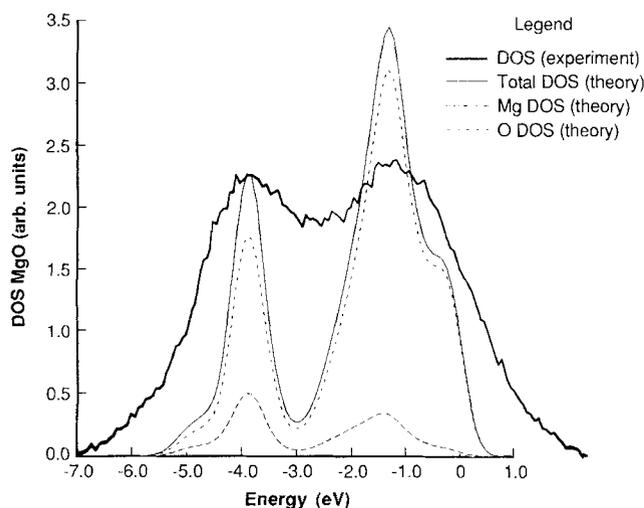


Fig. 3. Comparison of the O 2p upper valence bandwidth determined experimentally from valence band XPS and calculated for $(\text{MgO})_4$ at room temperature.

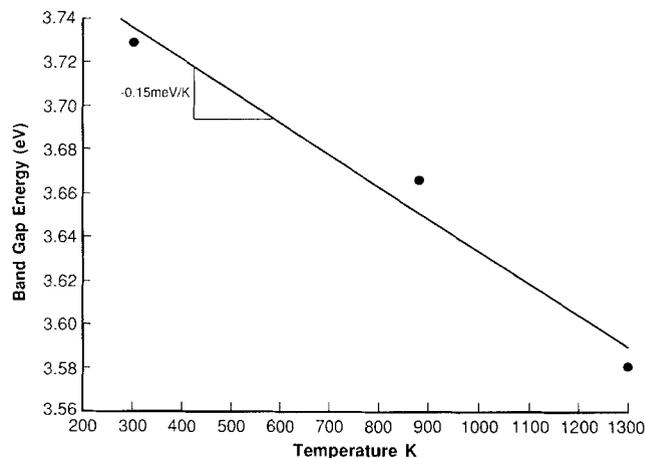


Fig. 4. Band gap energy of $(\text{MgO})_4$ as a function of pure thermal lattice expansion from 300 to 1300 K.

cific direction cosines such that the Mg-O bond lengths did not decrease because of the phonon vibration. These modes were a type of relaxation or sliding mode, as shown for mode E in Fig. 6, in which the phonon displacements of 0.16 Å are normal to the Mg-O nearest-neighbor bond directions. Both of these modes led to large decreases in the band gap. Mode E led to a band gap decrease of -0.95 eV. This mode, occupied with phonons to a displacement of 0.16 Å, produces a contribution to the band gap temperature dependence of -0.95 meV/K from room temperature to 1300 K.

From our direct calculations of the effects of thermal lattice expansion and the manifold of our electron-phonon calculations, we find that theoretically the band gap temperature dependence of MgO is -1.1 meV/K; -0.15 meV/K arises because of thermal expansion of the lattice while the majority of the band gap temperature dependence (-0.95 meV/K) arises because of the electron-phonon interaction.

We have taken an approach here of calculating individual electron-phonon couplings. A method of calculating the complete electron-phonon interaction, encompassing the simultaneous effects of all excited phonon modes on the electronic structure, would be a better way to model the complete band gap temperature dependence. In addition, with a more complete understanding of the phonon structure of the material, the normal modes and their specific occupancy and atomic displacements at temperature will give more quantitative electron-phonon coupling constants. Also by sampling the complete \mathbf{k} space band structure of the high-temperature electron-phonon system, instead of just the minimum band

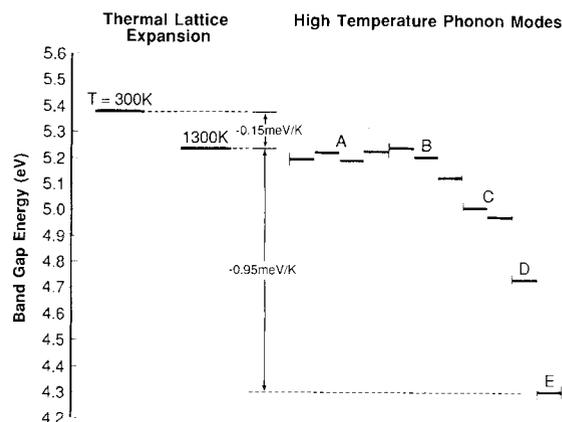


Fig. 5. Changes in the band gap of $(\text{MgO})_4$ shown for thermal lattice expansion from 300 to 1300 K and for each of the phonon modes calculated.

Phonon Modes

	Ion	Displ.	Dir.	MgO-O Bond Length	
A	Mg	0.16 Å	<111> <111> random sets of direction cosines	1.97-2.04 Å	
	O	fixed			
B	Mg	0.08 Å	<111> <111> random sets of direction cosines	1.99-2.16 Å	
	O	0.08 Å			
C	Mg	0.16 Å	<111> <111> random sets of direction cosines	1.94-1.96 Å	
	O	0.16 Å			
D	Mg	0.16 Å	<100> <100> specific sets of direction cosines	2.13 Å	
	O	0.16 Å			
E	Mg	0.16 Å	<110> <110> specific sets of direction cosines	2.15 Å	
	O	0.16 Å			

Fig. 6. Phonon modes used in the electron-phonon interaction band structure calculations.

gap energy, more detailed information on the individual phonon-induced shifts and dispersion changes of individual valence and conduction bands can be determined. Approaches of these sorts are now being pursued.

IV. Conclusions

The temperature dependence of the band gap of MgO has been modeled using an ab initio pseudofunction band structure calculations of a (MgO)₄ supercell, considering both lattice dilatation and individual phonon modes excited to the mean square thermal vibration amplitude, so as to determine the effects of thermal lattice expansion and the electron-phonon interaction.

The band structure calculated at room temperature is in good agreement with valence band X-ray photoemission results for the O 2p upper valence bandwidth. The band effective masses and band gap deformation potential of MgO are also determined.

Vacuum ultraviolet reflectance measurements find the band gap temperature dependence of single-crystal MgO to be -1 meV/K from 300 to 1300 K. Thermal lattice expansion is calculated to contribute -0.15 meV/K to the temperature dependence. The electron-phonon interaction is modeled using distorted lattice calculations for individual <111>, <100>, and <110> types of phonon modes. The <111> modes do not show strong electron-phonon coupling, which seems to correlate with the large decreases in the Mg-O nearest-neighbor bond length decreases and the high-energy nature of these modes. <100> and <110> modes, chosen so the Mg-O bond lengths do not decrease, exhibit strong electron-phonon coupling and

produce large decreases in the band gap. The manifold of results for the 10 electron-phonon calculations demonstrate an electron-phonon contribution to the band gap temperature dependence of -0.95 meV/K. These calculations give us new insight into the relative contributions of thermal lattice expansion and the electron-phonon interaction to the band gap temperature dependence, and the relative electron-phonon coupling for various phonon modes.

References

- R. H. French, R. L. Coble, R. V. Kasowski, and F. S. Ohuchi, "Vacuum Ultraviolet, Photoemission and Theoretical Studies of the Electronic Structure of Al₂O₃ up to 1000°C," *Physica B*, **150**, 47-49 (1988).
- R. H. French and J. B. Blum, "Electronic Structure and Conductivity of Al₂O₃," pp. 111-34 in *Ceramic Transactions*, Vol. 7, Sintering of Advanced Ceramics. Edited by C. A. Handwerker, J. E. Blendell, and W. Kayser. American Ceramic Society, Westerville, OH, 1990.
- R. H. French, "Electronic Structure of α-Al₂O₃, with Comparison to AlON and AlN," *J. Am. Ceram. Soc.*, **73** [3] 477-89 (1990).
- M. L. Cohen and D. J. Chadi, *Handbook of Semiconductors*, Vol. 2, Optical Properties of Solids; p. 155. North-Holland, New York, 1980.
- P. Lautenschlager, M. Garriga, and M. Cardona, "Temperature Dependence of the Interband Critical Point Parameters in InP," *Phys. Rev. B*, **36** [9] 4813-20 (1987).
- C. K. Kim, P. Lautenschlager, and M. Cardona, "Temperature Dependence of the Fundamental Energy Gap in GaAs," *Solid State Commun.*, **59** [12] 797-802 (1986).
- P. B. Allen and M. Cardona, "Theory of the Temperature Dependence of the Direct Gap of Germanium," *Phys. Rev. B*, **23**, 1495 (1981); "Errata," *ibid.*, **24**, 7479 (1981).
- P. B. Allen and M. Cardona, "Temperature Dependence of the Direct Gap of Si and Ge," *Phys. Rev. B*, **27** [8] 4760-69 (1983).
- G. Guizzetti, L. Nosenzo, and E. Reguzzoni, "Optical Properties and Electronic Structure of Alkali Halides by Thermoreflectivity," *Phys. Rev. B*, **15**, 5921-26 (1977).
- T. Tomiki, T. Miyata, and H. Tsukamoto, "Temperature Dependence of the Fundamental Spectra of Potassium Halides in the Schumann Ultraviolet Region (4.4-13.5 eV)," *J. Phys. Soc. Jpn.*, **35**, 495-507 (1973).
- R. V. Kasowski, T. N. Rhodin, M. H. Tsai, and D. D. Chamblis, "Pseudofunction Method: Application to a Monolayer of CO and to the Si (100) Surface," *Phys. Rev. B*, **34**, 2656-59 (1986).
- R. V. Kasowski, T. N. Rhodin, and M. H. Tsai, "Chemisorptive Bonding of Carbon Monoxide on Ni (001), Formulations and Application of a New Pseudofunctional Electron Muffin Tin Approach," *Appl. Phys. A*, **41**, 61-73 (1986).
- R. V. Kasowski, M. H. Tsai, and R. N. Rhodin, "Structural and Electronic Properties of a CO Monolayer," *Solid State Commun.*, **59**, 57-60 (1986).
- J. C. Slater, "Electronic Energy Bands in Metals," *Phys. Rev.*, **45**, 794-801 (1934).
- J. C. Slater, "Wavefunctions in a Periodic Potential," *Phys. Rev.*, **51**, 846-51 (1937).
- O. K. Andersen, "Linear Methods in Band Theory," *Phys. Rev. B*, **12** [8] 3060-83 (1975).
- M. L. Bortz, R. H. French, D. J. Jones, R. V. Kasowski, and F. S. Ohuchi, "Temperature Dependence of the Electronic Structure of Al₂O₃, MgAl₂O₄, and MgO," in *Proceedings of the Ninth International Vacuum Ultraviolet Radiation Physics Conference*, Hawaii, *Phys. Scr.*, **41** [4] 537 (1990).
- X. Zhu, S. Fahy, and S. G. Louie, "Ab Initio Calculation of Pressure Coefficients of Band Gaps of Silicon: Comparison of the LDA and Quasiparticle Results," *Phys. Rev. B*, **39** [11] 7840-47 (1989); (E) *ibid.* **40** [8] 5821 (1989).
- L. P. Bouckaert, R. Smoluchowski, and E. Wigner, "Theory of Brillouin Zones and Symmetry Properties of Wave Function in Crystals," *Phys. Rev.*, **50**, 58-67 (1936).
- R. M. Hazen, "Effects of Temperature and Pressure on the Cell Dimension and X-ray Temperature Factors of Periclase," *Am. Mineral.*, **61**, 266-71 (1976).
- R. H. French, "Vacuum Ultraviolet Spectroscopy of Ceramics"; pp. 406-14 in *Ceramic Transactions*, Vol. 5, Advanced Characterization Techniques for Ceramics. Edited by W. S. Young, G. L. McVay, and G. E. Pike. American Ceramic Society, Westerville, OH, 1989.
- R. H. French, "Laser-Plasma Sourced, Temperature Dependent VUV Spectrophotometer Using Dispersive Analysis"; in *Proceedings of the Ninth International Vacuum Ultraviolet Radiation Physics Conference*, Hawaii, *Phys. Scr.*, **41** [4] 404 (1990).
- H. Song, R. H. French, and R. L. Coble, "Effect of Residual Strain on the Electronic Structure of Al₂O₃ and MgO," *J. Am. Ceram. Soc.*, **72** [6] 990-94 (1989). □