Electronic density of states for the perovskites*

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It is shown that the density of states including all of the 14 primary conduction and valence bands of crystals with the perovskite structure can be derived from simple analytic functions of dimensionless variables. Good quantitative agreement with recent energy-band calculations is demonstrated for the electronic density of states of ReO_3, $SrTiO_3$, $KTaO_3$, and $NaWO_3$.

The density of states (DOS) of a solid is of fundamental importance in determining its electronic, transport, and optical properties. The DOS of crystals having the ABO_3 cubic perovskite structure (with B equal to a transition metal ion) is unusual in that it displays van Hove singularities characteristic of two-dimensional energy bands due to the symmetry of the interaction between d orbitals of the B ion and the p orbitals of the oxygen ions.

In a previous letter[1] we showed that the DOS of the three lower conduction bands could be derived quantitatively from a simple analytical function and that the two-dimensional character of these bands accounted for structure observed in optical reflectivity experiments[2] on $BaTiO_3$ and $SrTiO_3$. The 2-d character of these bands also produces a large Kohn effect in the phonon spectrum of the sodium tungsten bronze[3] ($NaWO_3$).

In this letter we show that the *total DOS including all 14 primary valence and conduction bands* can be derived from two simple universal functions of dimensionless variables. Thus we have reduced the DOS of the perovskites to an irreducible or universal form. The theory provides a simple interpretation of all of the DOS structure and yields DOS curves over a 15-eV range which are in good *quantitative* agreement with numerical histograms constructed from energy-band calculations for ReO_3, $SrTiO_3$, $KTaO_3$,[4] and $NaWO_3$.[5] These results are the only known example in which the energy bands and DOS of real compounds have been quantitatively described by closed form analytical formulas.

The simple linear combinations of atomic orbitals (LCAO) model and the corresponding energy bands of the perovskites have been described in detail in our previous papers.[1,6,7] These bands are derived from the interaction of the five d orbitals of the transition metal ion with the nine p orbitals of the three oxygen ions in each unit cell. It has been demonstrated that the most important parameters are the nearest-neighbor transfer integrals denoted by $pd\sigma$ and $pd\pi$. The energy bands involving

the states of the A ion are at energies much further removed from the band-gap region and have a negligible effect on the 14 primary bands described here. The effect of the oxygen-oxygen interactions will be discussed later in this paper.

The three d orbitals of t_{2g} symmetry interact through the $pd\pi$ parameter with the six p orbitals having their lobes oriented perpendicular to the B–O axis to form nine energy bands characterized as follows: three equivalent "π^*" conduction bands, three equivalent "π" valence bands, three equivalent "$\pi°$" nonbonding bands. The π and π^* bands can be expressed in terms of the universal function

$$\epsilon_\pi = -(C_\alpha + C_\beta) \quad (\alpha\beta = xy, yz, \text{ and } zx),$$
$$C_\alpha = \cos(2k_\alpha a), \tag{1}$$

where k_α is the αth component of the wave vector, a is the B–O bond length, and the dimensionless energy ϵ_π is given in terms of the real energy E by the expression

$$\epsilon_\pi = [(E - E_m)^2 - (\tfrac{1}{2}E_g)^2]/(pd\pi)^2 - 2. \tag{2}$$

In Eq. (2) E_m is the energy at the center of the gap between the conduction and valence bands and E_g is the energy gap. Solution of Eq. (2) for the energy E yields both the π and π^* bands. The universal DOS function associated with the bands of Eq. (1) is given (exact) by

$$\rho_\pi(\epsilon_\pi) = (1/\pi^2)K\{[1 - (\tfrac{1}{2}\epsilon_\pi)^2]^{1/2}\}\Theta[1 - (\tfrac{1}{2}\epsilon_\pi)^2], \tag{3}$$

where K is the complete elliptic integral of the first kind and $\theta(x) = 1$ for $x > 0$ and 0 otherwise. To obtain the DOS $\rho_\pi(E)$ for a particular perovskite one need only multiply $\rho_\pi(\epsilon_\pi)$ by the factor $|E - E_m|/(pd\pi)^2$. The quantity $\int \rho_\pi(E)dE$ integrated over all $E > E_m$ (or $E < E_m$) is unity.

The two d orbitals of e_g symmetry interact through the $pd\sigma$ parameter with the three p orbitals which have their lobes parallel to the B–O axis to form five energy bands characterized as follows: two distinct "σ^*" conduction bands, two distinct "σ" valence bands, one nonbonding "$\sigma°$" band.

The σ and σ^* bands are described by the universal function

$$\epsilon_\sigma = -(C_x + C_y + C_z)$$
$$\pm (C_x^2 + C_y^2 + C_z^2 - C_x C_y - C_y C_z - C_z C_x)^{1/2} , \quad (4)$$

where the dimensionless energy is related to the real energy by

$$\epsilon_\sigma = \frac{[E - E_m - \frac{1}{2}(\Delta_d + \Delta_p)]^2 - \frac{1}{4}[E_g + \Delta_d - \Delta_p]^2}{(pd\sigma)^2} - 3 . \quad (5)$$

In Eq. (5) $\Delta_d = E_{\sigma*} - E_{\pi*}$ and $\Delta_p = E_\pi - E_\sigma$ are the band splittings at the center of the Brillouin zone. The corresponding universal DOS function is given approximately by

$$\rho_\sigma(\epsilon_\sigma) = (1/\pi^2)(C + K\{[1 - (\tfrac{1}{3}\epsilon_\sigma)^2]^{1/2}\})\theta[1 - (\tfrac{1}{3}\epsilon_\sigma)^2]$$
$$- (1/\pi)^2(1 - \epsilon_\sigma^2)^{1/2}K[(1 - \epsilon_\sigma^2)^{1/2}]\,\theta(1 - \epsilon_\sigma^2), \quad (6)$$

$$C = \tfrac{1}{6}\{K^2(\tfrac{1}{2}\sqrt{2}) + \tfrac{1}{4}\pi^2[2 + 1/K^2(\tfrac{1}{2}\sqrt{2})]\}_| \simeq 1.515 .$$

$\rho_\sigma(\epsilon_\sigma)$ may be converted to $\rho_\sigma(E)$ by multiplying by the factor $2|E - E_m - 1/2(\Delta_d + \Delta_p)|(pd\sigma)^{-2}$ and the quantity $\int \rho_\sigma(E)dE$ integrated over $E \geq E_m$ (or $E \leq E_m$) is 2 because two conduction (valence) bands are described in Eq. (6). Equation (6) is a convenient approximation which was developed from consideration of the analytic character of the function in Eq. (4). It produces a DOS which is in error by less than 3% for any value of $-3 \leq \epsilon_\sigma \leq 3$. The jump discontinuities at $\epsilon_\sigma = \pm 3$ are due to the regions in k space where the bands are flat.

For the nearest-neighbor LCAO model the nonbonding bands are flat and the DOS functions are simply δ functions located at the top of the valence band at $E = E_\pi$ and at $E = E_\sigma$ for the π^0 and σ^0 bands, respectively. The major effect of oxygen-oxygen interactions is to broaden these δ functions into narrow peaks whose width is approximately equal to the LCAO parameters $pd\pi$ and $pd\sigma$ for the π^0 and σ^0 bands, respectively. Thus, we use

$$\rho_{(\pi^0_{\sigma^0})}(E) = (\lambda/\pi)^{1/2} \exp[-\lambda(E - E_{(\pi^0_{\sigma^0})})^2] . \quad (7)$$

The total DOS of a perovskite in units of states/ (spin cell energy) is given by

$$\rho_T(E) = 3\rho_\pi(E) + 2\rho_\sigma(E) + 3\rho_{\pi^0}(E) + \rho_{\sigma^0}(E) . \quad (8)$$

In Fig. 1 we show graphs of the dimensionless DOS functions from which the total DOS is derived. In Figs. 2 and 3 we present comparisons of the theoretical expression [Eq. (8)] with numerical histograms for the DOS of a number of d-band perovskites. The histograms for SrTiO$_3$, KTaO$_3$, and ReO$_3$ are from the calculations of Mattheiss[4] and the histogram for NaWO$_3$ is from the work of
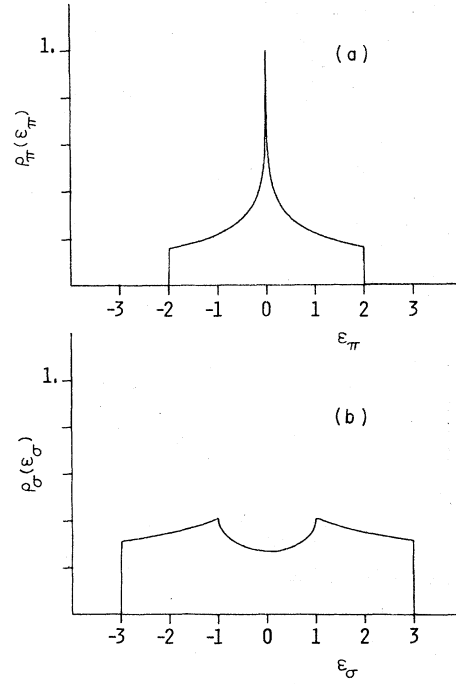

FIG. 1. Universal DOS functions for the energy bands of cubic perovskite crystals. (a) $\rho_\pi(\epsilon_\pi)$ from Eq. (3), (b) $\rho_\sigma(\epsilon_\sigma)$ from Eq. (6).
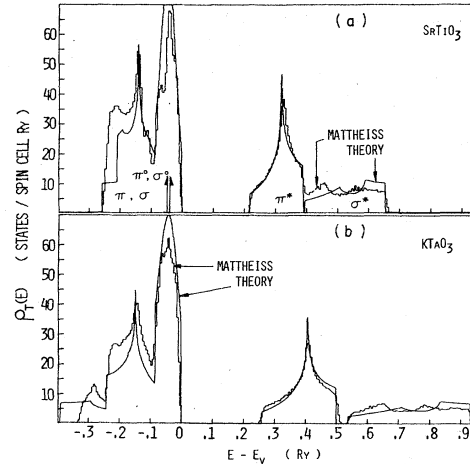

FIG. 2. Comparison of the theoretical DOS with numerical histograms for (a) SrTiO$_3$ and (b) KTaO$_3$. The histrograms are from the work of Mattheiss, Ref. 4. The parameters used (in Ry units) are (a) $E_g = 0.256$, $\Delta_d = 0.177$, $\Delta_p = 0.0375$, $(pd\pi) = 0.096$, $(pd\sigma) = -0.169$, and $\lambda = 907$ Ry^{-2}; (b) $E_g = 0.258$, $\Delta_d = 0.280$, $\Delta_p = 0$, $(pd\pi) = 0.123$, $(pd\sigma) = -0.247$, and $\lambda = 452$ Ry^{-2}. The contributions from the different bands and the location (arrows) of the π^0 and σ^0 bands are indicated. E_v is the energy at the top of the valence band.
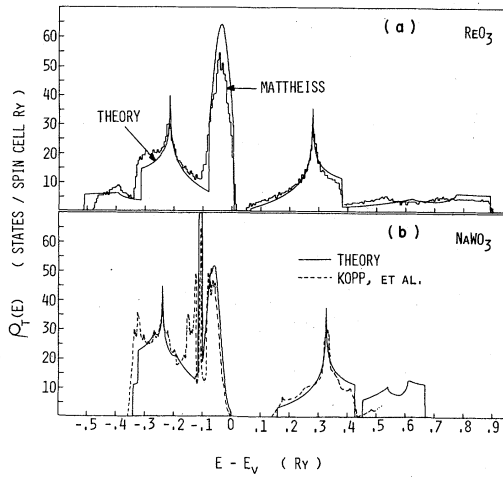
FIG. 3. Comparison of the theoretical DOS with nume-
rical histrograms for (a) ReO_3 and (b) $NaWO_3$. The
histogram for ReO_3 is from the work of Mattheiss, Ref.
4. The histogram for $NaWO_3$ is from the work of Kopp
et al., Ref. 5. The parameters used (in Ry units) are
(a) $E_g = 0.065$, $\Delta_d = 0.315$, $\Delta_p = 0$, $(pd\pi) = 0.122$, $(pd\sigma)$
$= -0.276$, and $\lambda = 452$ Ry^{-2}; (b) $E_g = 0.231$, $\Delta_d = 0.295$,
$\Delta_p = 0.036$, $(pd\pi) = 0.129$, $(pd\sigma) = -0.167$, and $\lambda_{\pi 0} = 925$
Ry^{-2}, and $\lambda_{\sigma 0} = 1.85 \times 10^4$ Ry^{-2}.

Kopp *et al.*[5]

The quantitative agreement between our theory
and the histograms from numerical energy-band
calculations is quite good, especially considering
the simplicity of the theory and the complexity of
the solids described. The major discrepancies,
evident at the bottom of the σ band and at the top
of the σ^* band, result from the neglect of the
oxygen-oxygen interactions in representing these
bands.

Equation (8) can be used to construct *a priori* a
reasonably accurate DOS for any cubic d-band
perovskite if estimates of the fundamental param-
eters E_g, $pd\pi$, $pd\sigma$, Δ_d, Δ_p, and λ can be made.
The shape of the DOS is independent of E_m. In
many cases the required parameters can be in-
ferred from experimental data or estimated from
information available in the literature. Our theory
therefore provides a simple analytical form for the
DOS that should be of value in interpreting the
electronic and optical properties of the perovskites.

Alternately, all of the parameters necessary to
construct ρ_T can be obtained from an energy-band
calculation of the states at a single point in the
Brillouin zone; for example, the X, M, or R point,
but not the Γ point.

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(2) should read $G(E) = (\xi/\pi)|E - \frac{1}{2}(E_t + E_\perp)|K(\xi)/(pd\pi)^2$
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