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ENERGY BAND CHANGES IN PEROVSKITES DUE TO LATTICE POLARIZATION

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(Received 28 February 1967)

Many perovskites are capable of a ferroelectric transition from a cubic to a tetragonal phase. This transition is accompanied by movements of the ions within a single unit cell relative to one another. This lattice polarization causes splitting and shifting of the critical points of the cubic band structure. Recently several authors[1,2] have suggested that a similar polarization may be caused by external electric fields, and a preliminary estimate of the magnitude of this effect has been made for the single critical point $X_{5'}^{\text{lower}} \to X_5$.

Here a more complete analysis of the polarization dependence of the Kahn-Leyendecker[3] LCAO band scheme for $SrTiO_3$ is considered. It takes into account the reduction of point group symmetry from O_h to C_{4v} which occurs when the ions are moved along an [010] direction. This lower symmetry allows some of the matrix elements between the tight-binding states to be nonzero which were zero in the undistorted situation. These new matrix elements which break the cubic symmetry are of two types. One of these is nonzero because of the changes that the displacements introduce in the cubic LCAO parameters $pp\pi$, $pp\sigma$, $pd\pi$, and $pd\sigma$. These changes were estimated by assuming, e.g., for $pd\pi$,

$$pd\pi = (pd\pi)_0 S/S_0,$$

where S is the overlap integral between Watson's analytic Hartree-Fock wave functions[4] and subscripts indicate evaluation for the cubic configuration. Further discussion of this approximation is referred to by Kahn and Leyendecker.[3] The other type arises because the lines joining various pairs of atoms are no longer mutually perpendicular. These matrix elements contain as a factor the cosine of the angle between bonds (an angle near $\frac{1}{2}\pi$) and so vanish as the bonds become orthogonal. All these matrix elements were evaluated in the two-center approximation of Slater and Koster.[5]

One result of the lower symmetry of the distorted case is that the X points and also the M points split into two sets for which the group of the wave vector is different. Taking the direction of the displacements as [010], the [100] and [001] X points are labled $X_\perp$ and the [101] M point is labeled $M_\perp$. The other points are labeled $X_\parallel$ and $M_\parallel$. It is then found that the lines $\Gamma \to X_\parallel$ and $M_\perp \to R$ have the full point group symmetry C_{4v} and hence have representations Δ_j and T_j. From $X_\perp \to M_\parallel$ the symmetry is C_{2v} and the representations are Z_j. For $\Gamma \to X_\perp$ and $X_\parallel \to M_\parallel$ the only symmetry operation aside from the identity is a single reflection plane—the xy or else the yz plane—and the representations are labeled G or U depending on whether they are even or odd under reflection. Symmetry then dictates the selection rules listed in Table I in the notation of Bouckaert, Smoluchowski, and Wigner and Hamermesh.[6]

Although the LCAO parameters used in Table I are for $SrTiO_3$, a very similar band structure should apply to $BaTiO_3$.[3] To gain some idea of the band structure for tetragonal $BaTiO_3$, the atomic displacements were chosen to correspond to this material.[7] The resulting band structure is compared with the cubic Kahn-Ley-

Table I. Selection rules dictated by the lower symmetry of the distorted case.

Polarization	Transition	Point
[100]	$\Delta_5 \leftrightarrow \Delta_1, \Delta_{1'}, \Delta_2, \Delta_{2'}$	$\Gamma, X_\parallel$
	$T_5 \leftrightarrow T_1, T_{1'}, T_2, T_{2'}$	$M_\perp$
	$Z_1 \leftrightarrow Z_3$ $Z_2 \leftrightarrow Z_4$	$M_\parallel[110]$ $X_\perp[100]$
	$Z_1 \leftrightarrow Z_4$ $Z_2 \leftrightarrow Z_3$	$M_\parallel[011]$ $X_\perp[001]$
[010]	Only between levels of the same symmetry type	All points

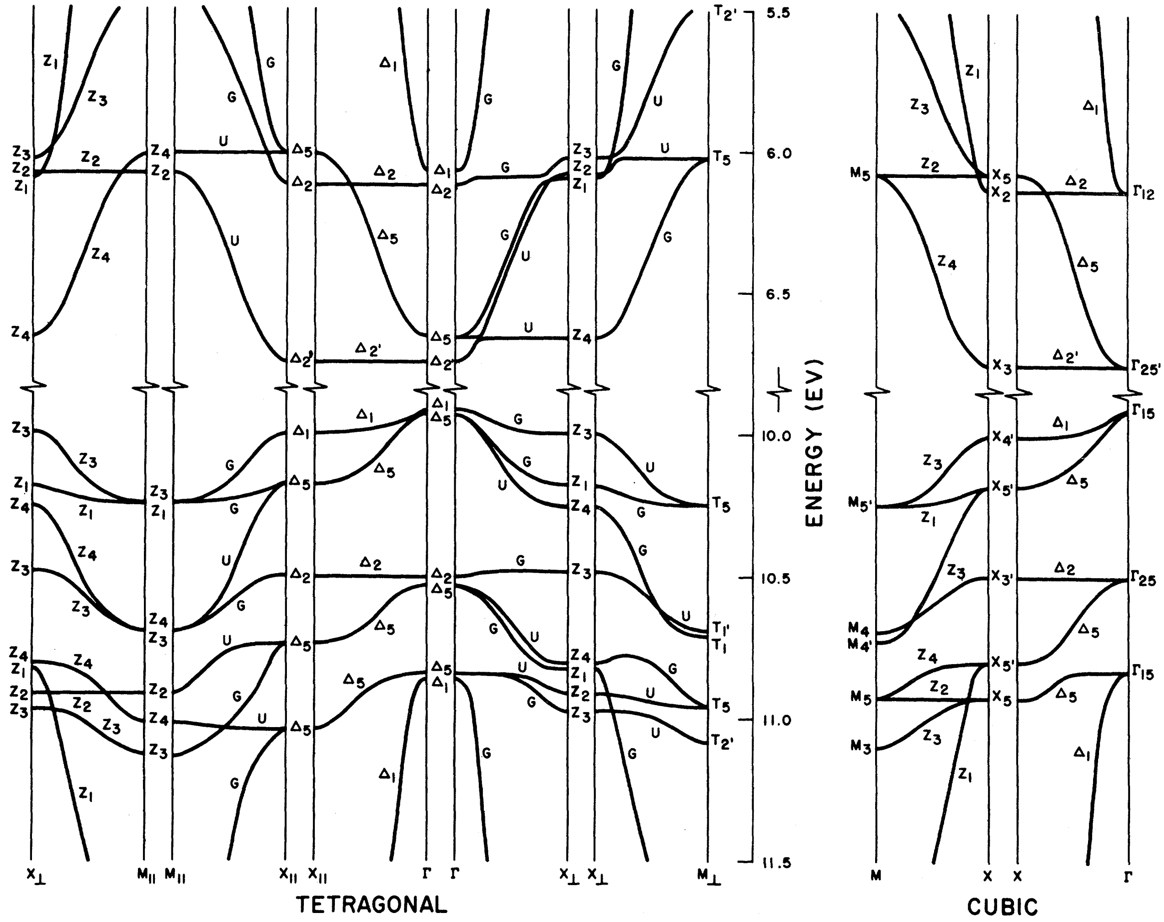

FIG. 1. Comparison of cubic with tetragonal band structure for ionic displacements found in $BaTiO_3$.

endecker band structure in Fig. 1. Several features should be noted:

(1) A number of levels have been split. Perhaps the most important of these is the splitting of $\Gamma_{25'}$. If the lowest energy transition in this material is $\Gamma_{15} \rightarrow \Gamma_{25'}$, under displacement a dichroism should appear since for [010] polarization the first transition is $\Delta_5 \rightarrow \Delta_5$ and for [100] polarization it is $\Delta_5 \rightarrow \Delta_{2'}$, which lies about 80 meV lower in Fig. 1. A dichroism of the right sign is observed in $BaTiO_3$.[8]

(2) A number of selection rules have been broken.

(3) The lowest conduction band is raised near X in directions normal to the axis of symmetry. Evidence for this has been reported by Berglund and Baer[9] in $BaTiO_3$.

(4) Finally the results for the $X_{5'}^{\text{lower}} \rightarrow X_5$ transition along the line $X_{\parallel} \rightarrow M_{\parallel}$ can be compared with those of Zook and Casselman.[2] They considered only the effect of variations in the $pd\pi$ LCAO parameter and also assumed that the displacement dependence of this transition was entirely due to movement of the X_5 point (one end of the flat Z_2 conduction band). In fact $X_{5'}$ also moves and the present calculation indicates that the transition has a quadratic dependence on displacement at low displacements as Zook and Casselman anticipated, but decreases in energy with increase in displacement instead of increasing as they suggested. For larger displacements this movement of the transition energy reverses until the transition occurs at almost its original energy for displacements of the size assumed for Fig. 1. Therefore the present model does not support the choice of this transition as the major source of the observed field dependence of the refractive index in these materials.[10] See Fig. 2. The Zook-Casselman analysis is really an approximate calculation of the curve $Z_2 \rightarrow Z_4$ in Fig. 2. In calculating the curves of Fig. 2 the

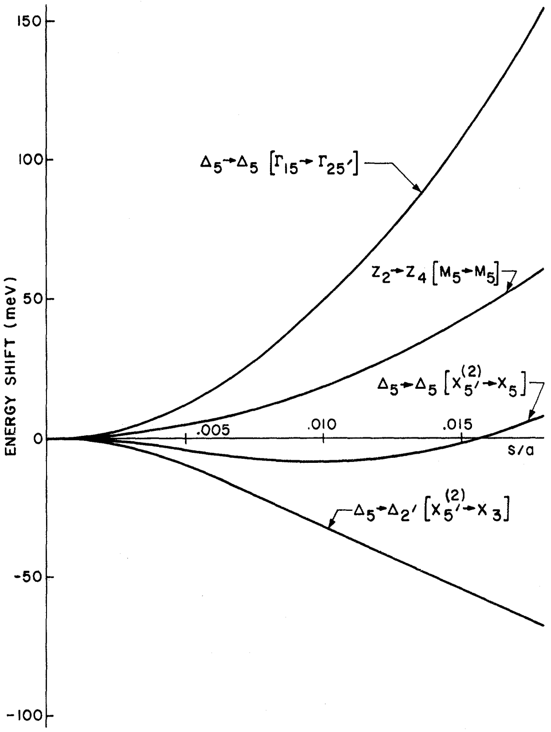

FIG. 2. Displacement dependence of several transitions in $SrTiO_3$. (s = displacement of the titanium atom, a = edge of unit cell.) Superscripts order levels of the same symmetry, increasing with distance from the band gap. The corresponding cubic transitions are in brackets. Data for any other transitions that may interest the reader are available.

ratios of the oxygen displacements to the titanium displacement s have been held fixed at the values of these ratios in tetragonal $BaTiO_3$. Hence the change in the Ti-O spacing along [010] $\Delta\rho$ is 2.5s. If $\Delta\rho$ is used as variable instead of s, the $Z_2 \to Z_4$ curve is not very different from the earlier result. (In comparing Fig. 1 with Ref. 2, it should be noted that the labeling of levels at $M_{\parallel}$ is determined by the higher symmetry along $X_{\perp} \to M_{\parallel}$. As a result, between $X_{\parallel}$ and $M_{\parallel}$ the flat Z_2 bands of the cubic case become the flat U levels terminating in Z_4 symmetry at $M_{\parallel}$.)

The author wishes to thank A. Frova for suggesting this problem and for suggesting some changes in presentation. Thanks also go to D. Kahng for his encouragement.

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