ments of Castle and Feldman.[11] It may be noted that even if the excess generated phonon population were larger than the number of absorbing spins, the principal heat-loss mechanism from the hot modes (after saturation of the spins) would still be transfer to the cold modes via spin scattering at the spin relaxation rate. This is considerably shorter than the rate for transfer via phonon-phonon scattering as estimated from microwave ultrasonic attenuation measurements.[12]

The original reason for undertaking this investigation was the observation, previously reported, that inversion of Fe^{2+} spins after rapid passage was not directly observable, and that this result was probably due to an extremely fast avalanche relaxation to saturation,[6] with a time constant 4×10^{-8} sec and a delay time (pedestal length) 3×10^{-7} sec.[13] The present observations support this conclusion. Indeed, if the avalanche could not occur in a time short compared with the propagation time through the emission volume into the absorbing region, there would be no avalanche formation at all.

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ELECTRO-OPTIC EFFECTS IN PARAELECTRIC PEROVSKITES

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Recent measurements[1-3] of the electro-optic (E-O) properties of four paraelectric perovskites ($SrTiO_3$, $KTaO_3$, $BaTiO_3$, and $KTa_{0.35}Nb_{0.65}O_3$), indicate that the E-O effect is determined by the polarization rather than the electric field. Since polarization is the fundamental variable, the E-O effect in these materials is not related to the Franz-Keldysh effect[4] which is a direct electric-field effect. The purpose of this Letter is to show that an estimate of E-O effect based on the change in electronic band structure with ionic displacements associated with the polarization is in reasonable agreement with experiment.

The E-O effect is describable in terms of the fourth-rank tensor coefficients, g_{11}, g_{12}, and g_{44}. The results for $KTa_{0.65}Nb_{0.35}O_3$ (KTN) can be summarized as follows:

$$\begin{aligned}\Delta n_{\parallel}/P^2 &\approx -1\ \mathrm{m}^4/\mathrm{C}^2,\\ \Delta n_{\perp}/P^2 &\approx 0,\end{aligned}\tag{1}$$

where $n_{\parallel}$ and $n_{\perp}$ are the indices of refraction for light polarized parallel and perpendicular to the static polarization, respectively. Equation (1) implies that the isotropy condition $g_{11}-g_{12}=g_{44}$ holds approximately. The second relation follows from $g_{12}\approx 0$. In the other materials the available data, while not complete, are so similar to the KTN result that it is reasonable to assume that (1) applies to all four materials.

The band structure of $SrTiO_3$ has been calculated by Kahn and Leyendecker (KL)[5] using the method of linear combination of atomic orbitals.[6] This is consistent with the measured optical properties[7] of $SrTiO_3$ and $BaTiO_3$ although a detailed comparison has not been made. The main peak in the reflectivity and in ϵ_2 occurs at 4.86 eV. The KL band structure indicates that there are quite a few transitions having energies near this value. As pointed out by Cardona,[7] the transition $X_{5'} \to X_5$ is a likely candidate. A detailed examination of the calculated band structure (see Fig. 1) shows that the transitions $Z_4 \to Z_2$ from about −10.90 to −6.35 eV (which become $X_{5'} \to X_5$ at the X point) are essentially independent of energy along the Z line, i.e., there is essentially a critical line rather than a critical point.[8] The index of refraction as a function of photon energy fits quite well to a single oscillator formula having about the same energy[7]:

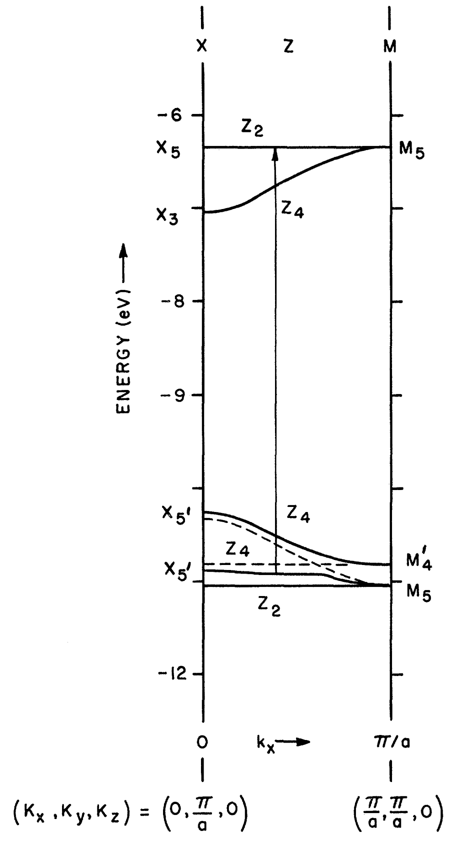

FIG. 1. Two of the five conduction bands and three of the nine valence bands are shown from the energy-band structure of KL (Ref. 4). X_5, Z_2, and M_5 refer to irreducible representations at the X, Z, and M points of the Brillouin zone (BZ). The dotted lines show the valence-band Z_4 levels in the absence of $(pp\sigma)$ and $(pp\pi)$ interactions. The arrow shows the transition $Z_4 \to Z_2$ to which we attribute the dispersion of the index of refraction and the E-O effect in the single oscillator approximation. The transitions $Z_2 \to Z_2$ and $Z_4 \to Z_4$ are forbidden.

$$n^2(\omega) = C_1 + C_2/(\omega_1^2 - \omega^2), \qquad (2)$$

where $C_1 = 3.16$,[9] $C_2 = 40\ \mathrm{eV}^2$, and $\omega_1 = 4.4$ eV.

Our calculation of the E-O effect is based on the following simplifying assumptions: (a) The change in the index of refraction is due to a change in the oscillator energy ω_1 associated with the transition $Z_4 \to Z_2$,[10] (b) the change in the Z_2 levels is due to the displacement of titanium with respect to oxygen ions on the Ti-O chains lying along a crystalline axis,[11] and (c) when the field-induced polarization is along a crystalline axis, the only ionic displacements are those of the Ti and O ions lying in O-Ti-O chains parallel to the polarization direction.[12] Because the $(pd\sigma)$ and $(pd\pi)$ energy overlap integrals[6] depend strongly on the Ti-O spacing, we expect changes in these overlap integrals to make the largest contribution to the changes in band structure.

The Z_2 levels on the (010) face of the Brillouin zone (BZ), for example, arise from a 2×2 secular determinant containing the square of the following off-diagonal matrix element in the KL notation:

$$\langle 0, z, 0 | H | yz \rangle = 2i(pd\pi) \sin k_y \rho, \qquad (3)$$

where ρ is the Ti-O spacing. When a field is applied along the y axis, these matrix elements squared are changed in the following way:

$$|\langle 0, z, 0 | H | yz \rangle|^2 = 4(pd\pi)^2 \sin^2 k_y \rho + 4(pd\pi) \frac{d^2(pd\pi)}{d\rho^2} \sin^2 k_y \rho (\Delta\rho)^2 + 4 \left| \frac{d(pd\pi)}{d\rho} \right|^2 \cos^2 k_y \rho (\Delta\rho)^2, \qquad (4)$$

assuming that the periodicity of the lattice stays the same, i.e., assuming no electrostriction. The change in energy of the upper Z_2 level is, then,

$$\Delta E_{Z_2} = \frac{4(pd\pi)}{E_{Z_2} - E_{Z_2}'} \frac{d^2(pd\pi)}{d\rho^2} (\Delta\rho)^2, \qquad (5)$$

where $E_{Z_2} - E_{Z_2}'$ is the splitting of the two Z_2 levels. The change $\Delta\rho$ in the Ti-O spacing in the O-Ti-O chains lying along the y axis changes the Z_2 levels on the (010) faces of the BZ, but causes no changes on the other faces of the BZ.

We have estimated the change of the overlap integrals with distance following the same approximation as that used by KL, i.e., assuming that the energy overlap integral is proportional to the wave-function overlap integral.[5,13] Using Watson's $\mathrm{Ti}^{+3}(3d)$ and $\mathrm{O}^{-2}(2p)$ Hartree-Fock wave functions,[14,15] we obtain for the wave-function overlap integrals

$$S_\sigma = -0.102\left\{1-1.33\frac{\Delta\rho}{\rho}-1.48\left(\frac{\Delta\rho}{\rho}\right)^2\right\}, \tag{6a}$$

$$S_\pi = -0.082\left\{1-3.14\frac{\Delta\rho}{\rho}+4.60\left(\frac{\Delta\rho}{\rho}\right)^2\right\}. \tag{6b}$$

Using (5) and (6b) and KL's value (0.84 eV) for $(pd\pi)$, we obtain

$$\Delta E_{Z_2}/(\Delta\rho/\rho)^2 \equiv b \approx +5.8 \text{ eV}. \tag{7}$$

In general the polarization is proportional to $\Delta\rho$ and we can write $P=P_0(\Delta\rho/\rho)$. Using assumption (c) and the effective charges[5] $q_{\mathrm{O}}=-1.7e$ and $q_{\mathrm{Ti}}=3.1e$, we obtain for $\mathrm{SrTiO_3}$

$$P_0 = 1.025e^2/a_0^2 = 0.98 \text{ C/m}^2,$$

where $a_0=2\rho=$ lattice constant. Therefore the energy shift divided by the polarization squared is

$$\Delta E_{Z_2}/P^2 \equiv a = b/P_0^2 = +6.0 \text{ eV m}^4/\text{C}^2. \tag{8}$$

This is a polarization potential, analogous to the deformation potential but with the polarization dyadic P_iP_j replacing the strain tensor S_{ij}. The polarization potentials for several optical transitions in $\mathrm{KTaO_3}$ can be estimated from the shift of electroreflectivity peaks with polarization measured by Frova and Boddy.[16] The largest peak, initially at 5.1 eV, shifted quadratically with polarization corresponding to a polarization potential of +29 eV $\mathrm{m^4/C^2}$. The other peaks shifted smaller amounts, and the dependence on polarization does not appear to be quadratic. Assuming similar results would be found in $\mathrm{SrTiO_3}$, our calculation for $\mathrm{SrTiO_3}$ agrees as to sign and order of magnitude.

To obtain an estimate of the E-O effect we equate ΔE in Eq. (8) with a change $\Delta\omega_1$ in Eq. (2):

$$\frac{\Delta n(0)}{P^2} \approx -\frac{C_2 a}{\omega_1^3 n(0)} \approx -1.2 \text{ m}^4/\text{C}^2. \tag{9}$$

Before comparing this number with experiment [Eq. (8)], we must look at the selection rules for the transitions $Z_4 \to Z_2$. Examination of the wave functions involved reveals that for the y polarization, the transitions occur only on the (010) faces of the BZ. Thus a polarization field along the y axis affects the optical transitions for light polarized along y (extraordinary ray) and it does not change the $(pd\pi)$ interaction on the (100) and (001) faces of the BZ, hence it does not affect the ordinary ray. Thus our estimate of Δn applies to $n_\parallel$, while we estimate $\Delta n_\perp \approx 0$. Our estimate is therefore in good agreement with experiment in explaining the sign, magnitude and anisotropy of the E-O effect.

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