netic parameter μ_I approaches β_I, implying confinement by the toroidal diamagnetic well. At the ultimate limit $\beta = 1$, $\beta_I = q^{2/3}\epsilon^{-4/3}$.

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Model of the Ferroelectric Phase Transition in the Tetragonal Tungsten-Bronze–Structure Ferroelectrics

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A microscopic model is presented for the ferroelectric phase transition in the tetragonal tungsten-bronze–structure ferroelectrics (e.g., $Sr_{1-x}Ba_xNb_2O_6$) which, for the first time, provides a description of its essential features, including the fact that it is a displacive transition but has no "soft"-phonon mode. The model employs an interaction between the ferroelectric phonon displacement and local structural changes, which are important in these materials; and it describes well important features of the Raman spectra, dielectric constant, and refractive index.

There is at present no basic understanding of the physical mechanism of the ferroelectric phase transition for the large class of technologically important ferroelectrics in the tetragonal tungsten-bronze $T1$ structure[1] [e.g., $Sr_{1-x}Ba_xNb_2O_6$ (SBN), and $Ba_{4+x}Na_{2-2x}Nb_{10}O_{30}$]. A model, which is based on the interaction of the ferroelectric phonon with specific local structural changes that are important in these disordered[2] materials, is presented and shown to account for this transition.

The tetragonal tungsten-bronze (TTB) $T1$ structure consists of a network of distorted NbO_6 octahedra [shown in Fig. 1(b)] connected together in such a way that there are pentagonal, square, and triangular "tunnels" which can be occupied by the Ba and Sr ions[2] of SBN. Ba and Sr ions are randomly distributed in the pentagonal tunnels, and Sr is randomly distributed in the square tunnels (but neither kind of tunnel is completely occupied). As the temperature is lowered through the ferroelectric T_c, the metallic atoms (including Nb) displace along the c axis into the oxygen layers.[2] Although this transition is displacive, it does not

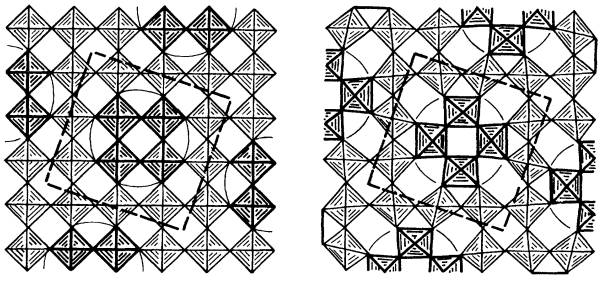

FIG. 1. Structure of tetragonal tungsten-bronze materials projected on the *ab* plane. Pentagonal, square (and triangular) cells contain Ba, Sr, Na, etc. ions. (a) is $T2$ phase and (b) is $T1$ phase. Square shows "unit cell" which is rotated in going from the $T1$ to the $T2$ phase.

conform to the soft-mode behavior.[3] Since the structural change is from C_{4v}^2 (ferroelectric phase) to D_{2d}^7 (paraelectric phase), it was proposed[1] that an A_1 soft mode should accompany the transition. However, detailed Raman (including polariton) measurements have failed to show evidence for any soft-phonon mode.[1,4] There are additional features of the transition which are not understood, which we discuss below.

The structures of these materials are unusual because there are various other structural phases separated from $T1$ by a small energy. Consider the structurally analogous material Na_xWO_3,[2] which is in the $T1$ phase for $0.2 \lesssim x \lesssim 0.45$ [Fig. 1(b)]. For $x \gtrsim 0.5$, it is in a cubic phase [similar to that in Fig. 1(a)]; and for $x \lesssim 0.2$, it is in a tetragonal $T2$ phase[2] [Fig. 1(a)]. An ideal geometrical operation[5] which takes the $T1$ structure into the $T2$ is a rotation of a square group of four corner-sharing octahedra through $\frac{1}{4}\pi$ radians as shown in Figs. 1(a) and 1(b), and it is repeated throughout the ab plane. From Figs. 1(a) and 1(b), it is seen that, locally, each group of four corner-sharing octahedra have (at least) two free-energy states corresponding to $T1$ and $T2$, with $T1$ being the ground state. We shall call the excitation between these two local energy states a "configurational-tunneling excitation" (CTE). Note that the rotation involves changes in electronic bonding (and does not result from a simple phonon condensation); therefore, there is a quantum-mechanical barrier between the local states.

The CTE and the model of the ferroelectric transition based on it are the novel concepts introduced in the present work. CTE's will have important physical effects in cases where they can be excited easily. We argue that they can be excited easily in the TTB ferroelectrics because (i) there is randomness in the occupation of cells by Ba and Sr, and thus there will be cells whose composition is very near that of the $T2$ (or the cubic) phase, and (ii) the bonding configuration of these materials differs from that of other configurations by a small amount of energy (since many structures are observed in isostructural compounds as a function of ion concentration and of temperature). Indeed, in the case of Na_xWO_3 for example, mixed $T1$ and $T2$ phases are observed for $0.12 \lesssim x \lesssim 0.28$, and mixed $T1$ and cubic phases for $0.38 \lesssim x \lesssim 0.43$.[2]

Consider now the ferroelectric transition in the present model. Because of occupancy randomness by Ba and Sr there are a substantial number of CTE's whose two energy states are nearly equal (nearly degenerate), and the ferroelectric A_1 phonon causes coupling between these two states. As the temperature is lowered, a local distortion of the A_1 phonon can occur accompanied by a splitting of the two CTE states (lowering $T1$ with respect to $T2$ locally) in a somewhat similar manner as in the pseudo-Jahn-Teller transition, e.g., in the rare-earth vanadates.[6] The phonon distortion is transmitted cooperatively through the system because of coupling between neighboring CTE's. Note that CTE is a different "degree of freedom" from any phonon and that the geometrical operation associated with a CTE primarily involves motions of ions in the ab plane whereas the A_1 displacement involves motion along the c axis. Note also that the ground state of the CTE remains the $T1$ state before and after the distortion.

The ferroelectric transition is given by the simplified model

$$H_i^{\mathrm{CTE}} = \tfrac{1}{2}\Delta_i \sigma_i^z + \tfrac{1}{2} g u_i \sigma_i^x, \qquad (1)$$

where the two levels of the ith CTE are spanned by the Pauli operators σ_i^{α} and g is the coupling constant of the CTE to the A_1-phonon displacement operator u_i.[7] The local A_1-phonon displacement is described by a harmonic Hamiltonian with a temperature-independent frequency. Note that the A_1 phonon distortion takes the system from the $T1$ phase to a distorted ferroelectric $T1$ phase, whereas σ^x takes the system (locally) from the $T1$ phase to the $T2$ phase. The $T2$ phase is unrelated to the $T1$ phase—whether distorted or not—and therefore coupling between a given phonon displacement and each component of σ^{α} is allowed.[7] The coupling in Eq. (1) is in part electrostatic; this arises because the CTE has a dipole moment, the existence of which can be inferred from the difference between the measured polarization and that calculated from the ionic displacements.[8]

We evaluate the contribution of the CTE to the free energy in a mean-field approximation in which u_i is taken to be its thermal average $\langle u_i \rangle$. This gives

$$F_i = -k_B T \ln[2\cosh(\lambda_i / 2k_B T)],$$

where $\lambda_i = (\Delta^2 + g^2 \langle u_i \rangle^2)^{1/2}$. The total free energy is $F_i^T = F_i + F_i^{\mathrm{ph}}$, where $F_i^{\mathrm{ph}} = C\langle u_i \rangle^2$ is the energy of the phonon distortion. Minimizing F_i^T with respect to $\langle u_i \rangle$ gives $2C\langle u_i \rangle = g^2 \langle u_i \rangle \lambda_i^{-1} \tanh(\lambda_i / 2k_B T)$, which has $\langle u_i \rangle \neq 0$ solutions for $T < T_c$, where T_c is given by $2C\Delta/g^2 = \frac{1}{2}\tanh(\Delta / 2k_B T_c)$. The phonon distortion is transmitted through the lattice via coupling between the CTE's of the form

$\vec{\sigma}_i \cdot \vec{\vec{J}}_{ij} \cdot \vec{\sigma}_j$. Contributions to J_{ij} include those from (i) dispersion in the A_1 phonon frequency $\omega_{\vec{k}}$ and in its coupling parameter $g(\vec{k})$ and (ii) direct (bonding) coupling between CTE's. For negligible randomness in Δ_i, dispersion in Eq. (1) gives[6]

$$J^{xx}(\vec{k}) \cong 2\omega_{\vec{k}}^{-1} |g(\vec{k})|^2 - 2N^{-1} \sum_{\vec{k}} \omega_k^{-1} |g(\vec{k})|^2.$$

Then the macroscopic ferroelectric distortion is $\langle u \rangle = -(2M\omega_{k=0}^2)^{-1} g(0) N^{1/2} \langle \sigma^x \rangle$, where M is the effective mass of the phonon, and $\langle \sigma^x \rangle$ is obtained by a straightforward mean-field treatment of the CTE-CTE coupling.[6]

Consider the effects of randomness in Δ_i and in the coupling J_{ij}^{xx} (including contributions from g_i). In the mean-field treatment,

$$\langle \sigma_i^x \rangle = [\textstyle\sum_j J_{ij} \langle \sigma_j^x \rangle / \Lambda_i] \tanh[\Lambda_i / k_B T],$$

where $\Lambda_i = [\Delta_i^2 + (\sum_j J_{ij} \langle \sigma_j^x \rangle)^2]^{1/2}$. When expanded[9] for small $\Lambda_i / k_B T$, this gives $k_B T \langle \sigma_i^x \rangle = \sum_j J_{ij} \langle \sigma_j^x \rangle$. This last equation is formally equivalent to the tight-binding Schrödinger equation for an electron with off-diagonal site disorder (where $k_B T$ corresponds to the energy and $\langle \sigma_i^x \rangle$ to the amplitudes of the Wannier functions) which has been treated in detail.[10] The equation above is also closely related to the mean-field treatment of the spin-glass system.[11] By recalling that $\langle u_i \rangle \propto \langle \sigma_i^x \rangle$, it is seen from these studies[10,11] that in the above approximation the present system has several well-defined phases: At sufficiently high temperatures, there exists a phase in which locally all $\langle u \rangle$ are zero (paraelectric I phase); at lower temperatures, there is a phase with spatially separated (uncorrelated) regions having $\langle u \rangle \neq 0$ (paraelectric II phase); and for sufficiently low temperatures, there is a phase with macroscopic reversible polarization (ferroelectric phase).[12] Detailed calculations of the boundaries between these phases have been given.[10,11] The temperature dependence of the size and number of regions with $\langle u \rangle \neq 0$ in the paraelectric II phase is given by the method of Ref. 10.

Consider now a variety of recent experimental results, the essential features of which are accounted for by the present model.

Raman spectra.—(1) The absence of a soft-phonon mode follows naturally from the model because in it the ferroelectric distortion occurs as a result of a pseudo-Jahn-Teller coupling of the ferroelectric A_1 phonon to the CTE's and not because of a soft-phonon mechanism.[3] The coupling between the optic A_1 phonon ($\omega_{A_1} \gtrsim 270\ \mathrm{cm}^{-1}$) and the spin-deviation–like mode[6] corresponding to the CTE levels (the frequency of which tends to zero at T_c) is very small because of the large difference in energy between ω_{A_1} and that of the spin-deviation mode for T near T_c. (2) Doping SBN with Nd^{+3} changes T_c dramatically but has negligible effect on the Raman spectra.[4] We note the presence of the large Nd^{+3} ions makes transitions between the local levels of the CTE more difficult [decreasing g in Eq. (1)] and thus decreases T_c. The phonons, which are vibrations about local minima, are largely unaffected by the doping. (3) Finally, the intrinsic relaxation of the CTE's will give a contribution to the quasi-elastic scattering which has been observed in the lowest E mode spectrum.

Low-frequency dielectric constant.—The low-frequency dielectric constant $\epsilon(\omega)$ of the TTB ferroelectrics given by the Lyddane-Sachs-Teller relation using the Raman phonon frequencies is independent of T, whereas capacitive measurements show a strong increase of $\epsilon(\omega)$ as $T \to T_c$ and also show frequency dispersion.[1,8] The self-consistent polarization[1] of the CTE's and the harmonic phonon displacements give

$$\epsilon(\omega) - \epsilon_{ph} = 4\pi[(\epsilon_{ph}+2)/3]^2 \{[\textstyle\sum_i \alpha_i(\omega, T)]^{-1} - (4\pi/3)[(\epsilon_{ph}+2)/3]\}^{-1},$$

where $\sum_i \alpha_i(\omega, T)$ is the sum of the polarizabilities of the CTE's, and ϵ_{ph} is the temperature-independent phonon contribution to $\epsilon(\omega)$ at low frequency in the absence of coupling to CTE's. If we take the polarizabilities of the CTE's to arise from thermally assisted hopping over their barriers U_i, then[13]

$$\textstyle\sum_i \alpha_i(\omega, T) = \sum_i \{(\Delta d_i)^2 / [4k_B T \cosh^2(\Delta_i / 2k_B T)]\} \times \{[1 + \omega^2 \tau_0^2 \exp(2U_i / k_B T)]\},$$

where Δd_i is the dipole-moment difference between the CTE states and τ_0 is a constant prefactor. Detailed measurements of $\epsilon(\omega)$ give information about Δ_i and U_i of the CTE's. For example, from the frequency dependence[8] of $\epsilon(\omega)$ for $Sr_{0.73}Ba_{0.27}Nb_2O_6$ at $T = 50°C$ ($T \lesssim T_c$), we estimate that the average value $\bar{\tau}(50°C) \cong 5 \times 10^{-7}$ sec; such a slow relaxation time is consistent with configuration tunneling as in the CTE. The CTE result for $\epsilon(0) - \epsilon_{ph}$ above accounts naturally for three important features of $\epsilon(0)$ (we consider $T \to T_c^-$ for definiteness): (i) ϵ increases as $T \to T_c^-$ because of the increased polarizabilities of the CTE's; (ii) as ω decreases, more barriers become accessible ($\omega \tau_i \lesssim 1$ for more τ_i), and $\epsilon(\omega)$ increases, as is observed[8] (this frequency dispersion is an important verification of the tunneling nature

of the CTE's; and (iii) as randomness (deviation from stoichiometry) increases, ϵ increases for fixed ω and T because of the increased number of CTE's, which is also observed.[1,8]

Refractive index.—The measured refractive index $n(T)$ of the TTB ferroelectrics is qualitatively different from "pure" ferroelectrics because it is a smoothly varying function of T for a wide interval of T near T_c.[1] In the paraelectric I phase, the model gives $n = n^{(0)}$, where $n^{(0)}$ is the high-temperature extrapolation of n. In the paraelectric II phase, $n - n^{(0)} \cong -\frac{1}{2}(n^{(0)})^3 g V^{-1}(e^*)^2 \times \sum_i u_i^2(T)$, where n is the refractive index along the c axis, g is the appropriate quadratic electro-optic coupling constant, e^* is the effective charge of a CTE, and the sum is taken over the regions in which $\langle u \rangle \neq 0$. In the "ferroelectric" phase, n goes over fairly smoothly to the form appropriate for no disorder.

The present model can be tested experimentally by noting that the local structural excitations will have many effects similar to those of the "tunneling modes" in glasses. For example, from the tunneling nature of the modes we predict power-dependent saturation of ultrasonic attenuation[14] [in addition to the frequency dispersion in $\epsilon(\omega)$ discussed above]. There will also be deviations from Debye-model predictions for the low-temperature heat capacity,[15] velocity of sound,[16] and nuclear spin-lattice relaxation.[17] The specific nature of the local structural excitations proposed here can be tested by doping the material with large ions like Nd^{+3} which will increase their excitation energies as discussed above.

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