Competing Interactions in Complex Ferroelectric Systems

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Abstract. In spite of the success of electron theories to account for the ferroelectric phenomena, ideas in classical crystal chemistry are still useful in unraveling complex behavior of multi-component solids. In particular they provide a natural explanation of high susceptibilities of mixed-ion systems based upon the concept of competing interactions. However, they are largely phenomenological and empirical. It is suggested that the concept of atomic level stresses can bridge the gap between the crystal chemistry approach and first-principle calculations in a most meaningful way. Also some novel experimental methods, which directly probe certain aspects of the electronic state relevant for this phenomenon, are discussed.

INTRODUCTION

A major progress was made in the field of ferroelectrics in the last decade, prompted by the successes in theoretical description and calculation of the atomic structure and electronic ground state [1], polarization [2,3], and thermal properties [4]. Undoubtedly the classical picture of rigid ions being displaced from the high-symmetry sites due to electro-static interaction has to give way to the modern quantum-mechanical description of the phenomenon based upon the change in the electronic ground state. In particular, it is now well understood that modulation of covalency which results in charge transfer between anions and cations is central to the occurrence of strong ferroelectricity.

However, a gap still exists between the first-principle calculations and the real ferroelectric materials, which are often very complex in structure. Simply increasing the size of the unit cell for the first-principle calculation does not appear to be sufficient. Instead, it is often suggested that this gap is best bridged by a crystal-chemistry (CC) approach, even though it is an empirical, phenomenological method and suffers from ambiguities and subjectivities. In our view the utility of the CC approach is not limited just to bridging the gap. The most important advantage of the CC approach is that it provides insights into the inner-workings and subtle details of the structure, and intuitively elucidates the properties of the solid, even though it is done at the expense of quantitative rigor. For instance the CC approach is better fitted to describe the internal conflicts among the forces acting in the solid, and to explain how high sensitiv-
ity of the solid to external fields could come about. In this paper we illustrate this point, using the examples of complex mixed-ion perovskites and experimental data by the pulsed neutron atomic pair-density function (PDF) method, and suggest the way in which the quantum-mechanical calculations provide rigorous foundation for this approach. In addition, we will discuss some new experiments that probe the electronic state and directly test theoretical calculations.

NATURE OF THE GROUND STATE

A fundamental philosophical difference exists on the nature of the ground state, between the crystal chemistry (CC) approach and the quantum-mechanical (QM) or first-principle approach. In the CC approach there is an “ideal” environment for each ion, and any deviation from it results in compromise and costs energy. For the discussion of ferroelectric oxides the ideal environment is usually described in terms of the ionic size or bond length, and electronic polarization due to asymmetric covalent bonds. On the other hand in the QM approach the structure of the ground state comes directly out of the calculation. In this view the concept of ionic size is irrelevant, since dividing the space between two kinds of ions is completely arbitrary and appears to be a senseless exercise. In the QM approach the ground state is the ultimately stable state, and usually no question is asked on the nature of the ground state. In the CC approach the ground state could be the result of compromises of competing forces, and depending upon the degree of compromises made there is a continuous grade of stability. We will first describe this difference more quantitatively, and suggest a method to reconcile the two approaches.

In the QM approach the total energy of the system is minimized with respect to the atomic positions, \( r_i \). The effective Hamiltonian for lattice dynamics [4] is obtained by expanding the energy by the local deviations from the equilibrium positions. The effective Hamiltonian approach was proposed indeed to bridge the gap mentioned above, but for the reason below it is not a substitute for the CC approach. On the other hand, the basis of the CC approach [5] is the conviction that the energy of the system can be expressed in terms of the pair-wise potential,

\[
V = \sum_{i<j} V_{ij}(r_{ij}),
\]

where \( r_{ij} \) is the separation between the \( i \)-th and \( j \)-th ions, and the ground state is obtained by minimizing the potential energy \( V \). At this stage alone, the superiority of the QM approach is obvious, since the existence of the interatomic potential that is transferrable from one compound to another is questionable.

However, if we go further into the analysis, the unique power of the CC approach becomes clear. Except in a simple system the interatomic distance in the ground state may not agree with the minimum of the potential (1), resulting the two-body force,

\[
f_{ij} = \frac{\partial V_{ij}}{\partial r_{ij}} \frac{r_{ij}}{r_{ij}}
\]
where the rotational force is neglected for the moment. Since the local sum of the forces,

\[ f_i = \sum_j f_{ij}, \]

is zero in the equilibrium structure, the presence of the force does not appear to have an immediate consequence. However, non-zero local forces produce a non-zero atomic level stress tensor [6],

\[ \sigma^{\alpha\beta}_i = \frac{1}{\Omega_i} \sum_j f_{ij}^\alpha \cdot r_{ij}^\beta, \]

where \( \alpha, \beta \) denote the cartesian components and \( \Omega_i \) is the local atomic volume and is included for the dimensionality purpose. For instance the pressure,

\[ p_i = \frac{1}{3} \text{Tr} \langle \bar{\sigma} \rangle, \]

will not be zero if the local volume does not fit the ionic size. The volume average of the atomic level stresses is equal to the macroscopic stress, which is zero for an isolated system. Then for a simple elementary solid the stress is zero everywhere, but in a complex system it is non-zero, and expresses the geometrical compromise necessary to construct the structure. For instance this concept was used in analyzing the local structure of glasses and their thermodynamics with much success [6,7]. Fig. 1 shows the distribution of the atomic level pressure calculated for a model metallic glass [7].

It is possible to calculate the local stress tensor quantum-mechanically, by using the Hellmann-Feynman force formula [8,9]. First, equation (4) can be expanded to the case of dynamic systems;

\[ \sigma^{\alpha\beta}_i = \frac{1}{\Omega_i} \left[ \sum_j f_{ij}^\alpha \cdot r_{ij}^\beta + M_i v_i^\alpha v_i^\beta \right]. \]

where \( M_i \) is the mass, and \( v_i \) the velocity, of the \( i \)-th atom. The quantum-mechanical equivalent of the local stress field is,

\[ \sigma^{\alpha\beta}(r) = \sum_n \langle \Psi | \left( r^\alpha_n \frac{dV}{dr^\beta_n} + \frac{p_n^\alpha p_n^\beta}{m_n} \right) | \Psi \rangle, \]

where \( \Psi \) is the many-body ground state wavefunction of the system, \( V \) is the interaction potential and \( \mathbf{p} \) is the momentum operator. The atomic level stress is defined by
Generally it is not easy to use the Hellmann-Feynman formula (7), since there are a lot of cancellations and many k-points have to be used in calculating the expectation value. With the advance in computational power this problem is becoming less of a barrier. Thus quantum-mechanical calculations can provide the foundation for the CC concept, and can bridge the two approaches. It is strongly recommended that such a calculation be done for some prototypical systems.

It is useful to relate the stress tensor to the effective Hamiltonian [4] of the lattice dynamics. The local force (2) may be expressed as,

\[ f_{ij} = A u_{ij} \frac{r_{ij}}{r_{ij}}, \quad A = \frac{\partial V_{ij}}{\partial r_{ij}} \bigg|_{r_0}, \quad u_{ij} = r_{ij} - r_0, \]  

where \( r_0 \) is the position of the minimum of \( V_{ij}(r) \). The coefficient \( A \) is related, though not identical, to the coefficients of the effective Hamiltonian. However, the effective Hamiltonian has no information regarding \( r_0 \), and this has to be supplied either empirically as in the CC approach, or through evaluating (7).

It should be noted that the atomic-level stresses thus defined are not zero even in crystalline solids, except for a Bravais lattice. The effect is clearly seen in an alloy system, \( \text{A}_1\text{x}\text{B}_x \). As \( x \) is changed the average interatomic distance changes from the A-A to B-B distance. Locally, however, the actual atomic distances are close to the expected A-A, A-B, or B-B distances, rather than the average atomic distance. This can be observed by local probes, such as the XAFS or atomic pair-density function (PDF) method. As shown in Fig. 2 [10] when an A atom is embedded in the system rich in B, the local A-B distance is closer to the ideal distance than the average distance, but the local stress causes a small deviation. This trivial example underscores the validity of the “ideal” bond length and the resulting atomic-level stresses.

**COMPETING FORCES**

**Ionic size and polarization**

We now discuss how the CC approach can elucidate the competing interaction and reaction of complex systems. The CC approach goes even further than the concept of the ideal bond length, to the idea of ionic size. Shannon and Prewitt [11] and Shannon [12] tabulated the empirically determined “ionic radius”, and suggested that the ideal bond length between two ions is obtained by simply summing the radii of each. This simple concept works remarkably well, to the dismay of QM physicists. The reason why it works well is that the interatomic distances are largely determined by the repulsive potential, which is a strong function of the interatomic distance.
In addition to the ionic size factor, the tendency for local polarization is an important element in the context of ferroelectricity. Some ions, such as Ti$^{4+}$ and W$^{6+}$, are polar, and become off-centered in the oxygen cage, for instance in BO$_6$ octahedron. The pulsed neutron PDF of WO$_3$ is shown in Fig. 3. The first peak corresponding to the W-O distances is split into two, at 1.78 Å and 2.05 Å, indicating local polarization of W$^{6+}$. Local polarization can be included in (1) through the core polarization potential in the shell-model [13]. Some of the A-site ions, notably Li$^+$ and Pb$^{2+}$, are also locally off-centered, due to asymmetric covalent bonds. In the case of Pb$^{2+}$ two lone-pair s-p electrons form covalent bonds with 3 or 4 oxygen ions, resulting in strong off-centering. It is well documented through the pulsed neutron PDF measurements that the amount of local off-centering of Pb is remarkably invariant, about 0.5 Å, in different compounds, even though the average structure may not indicate so [14].

**Tolerance factor**

The ionic radius, not only is a simple and useful tool to predict the atomic distances and the lattice constant, but also predicts details of the atomic structure. The
The most widely used concept derived from this approach is the tolerance factor of the structure. In the ideal perovskite, $ABO_3$, the A-O distance, $R_{A-O}$, is equal to $\sqrt{2}$ times the B-O distance, $R_{B-O}$. Thus, the tolerance factor defined as

$$t = \frac{R_{A-O}}{\sqrt{2}R_{B-O}}$$

is unity for the ideal structure. Deviation of $t$ from unity implies the competition between the AO sublattice and the BO$_2$ sublattice, which results in distortion of the perovskite structure. If $t < 1$, the BO$_6$ octahedra will become rotated, as is widely observed in many perovskites and related compounds. Since rotation of one octahedron leads to rotation of the neighboring octahedron in the opposite sense (zone-boundary phonon mode), it doubles the unit cell, and can result in the antiferroelectricity (AFE). Actually AFE usually results from this type of geometrical incompatibility. An example is PbZrO$_3$ ($t = 0.973$).

If $t > 1$, BO$_6$ can be polarized, usually resulting in ferroelectricity (FE). A classical case of the size-effect on ferroelectricity is the difference between BaTiO$_3$ (BT, $t = 1.06$), which is strongly ferroelectric, and SrTiO$_3$ (STO, $t = 1.002$), which is quantum-paraelectric [15]. Ti has room to be displaced in BT, but not in STO. This argument, of course, cannot be carried too far. The actual Ti displacement is larger than predicted by the size argument, and is definitely an electronic phenomenon. For PbTiO$_3$ (PT) the value of $t$ is 1.02, but since Pb is strongly polar PT is strongly ferroelectric.

### Mechanism of relaxor ferroelectricity

In mixed-ion oxides the local variations in ionic size and polarizability always produce local conflict to varying degrees, and result in complex behavior as a function of composition and temperature. A most conspicuous example is relaxor ferroelectricity. Strong disorder brought about by local incompatibility frustrates ferroelectricity, and results in a glass-like relaxor behavior, with strong parallel to the spin-glass phenomenon [16]. It is well known there are three origins for the spin-glass; 1) random exchange, 2) random field, and 3) random anisotropy. It should be noted that there is a critical value for the strength of disorder to produce the spin-glass or relaxor behavior. For instance, there is a critical ratio of the distribution width of the exchange constant, $\Delta J$, to the average, $<J>$, for the spin-glass behavior to prevail [17]. Theoretically a random anisotropy magnet is always a spin-glass, no matter how small the anisotropy is [18]. In practice, however, there is a threshold in the magnitude of anisotropy for rapid change of the behavior from a regular ferromagnet-like behavior to a spin-glass behavior [19,20].

The equivalents for the relaxor case are, 1) random mixture of FE and AFE, 2) random field, and 3) random anisotropy. Mixture of FE and AFE is achieved by mixing B-site ions with $t$ values greater than unity and less than unity [21]. An example is Pb(Zr$_{1-x}$Ti$_x$)O$_3$ (PZT) [22] and Pb(Sc$_{1/2}$Ta$_{1/2}$)O$_3$ (PST) [23]. In spite of the AFE tendency of PZ ($t = 0.973$) the FE tendency of PT ($t = 1.02$) and Pb polarizability wins over, making PZT an FE. However, locally PZT is very disordered [22]. In rhombo-
hedral PZT, even though the average symmetry dictates that the Pb polarization is along [111], locally it is close to [110]. In PST the AFE tendency is stronger, since $t = 0.953$ for PS and $t = 1.002$ for PTa. Because of this competition the local structure of PST is strongly deviated from the average structure as shown in Fig. 4 [24]. Locally Pb polarization is in [100] direction, but the direction of local polarization varies among the equivalent directions, for instance for PST (100), (010), and (001), resulting in the average polarization in the [111] direction.

Because of the local conflict in these compounds, small additional disorder can drive the system to a relaxor state. For PZT addition of a small amount of La$^{3+}$ (1.36 Å) yields relaxor PLZT. For PST B-site cation ordering produces regular FE, while the relaxor behavior is observed when B-sites are chemically disordered. In PMN the FE/AFE competition is weaker than in PST, since $t = 0.964$ for PM and 1.002 for PN, not strong enough to produce a relaxor state. Thus random mixture of B-sites by ions with different valences, Mg$^{2+}$ and Nb$^{5+}$, can produce random electric field at the A-site [25]. However, B-sites are occupied in average by 2.7 Mg and 5.3 Nb, so that the field gradient is better described by a crystal-field tensor with $l$ greater than 1, thus the random anisotropy model is better suited to describe the system than the random field model [14,26]. Also barriers exist for polarization to turn from one direction to another, and they are described by the anisotropy energy [14,26].

![FIGURE 4](image-url) Pulsed neutron PDF of Pb(Sc$_{1/2}$Ta$_{1/2}$)O$_3$ at T = 10 K (circles) compared to the PDF calculated for the crystal (average) structure determined by the Rietveld refinement [24], indicating significant local deviations.

**PROBING ELECTRONIC STRUCTURE**

The special electronic effects the QM calculations depict can be verified by various direct experimental methods. In this paper we will discuss two possible experiments involving x-rays. The first is the x-ray anomalous scattering to detect the electronic polarization, and the other is the x-ray inelastic scattering to measure the amount of charge transfer involved in the electron-phonon coupling.
X-ray anomalous scattering

The x-ray atomic scattering factor $f$ is dependent on the momentum transfer $Q$ as well as the incident photon energy $E_{pi}$;

$$f(Q, E_{pi}) = f_0(Q) + f'(E_{pi}) + if''(E_{pi}).$$ (11)

The $E_{pi}$ dependent part is called the anomalous dispersion, and is strongly dependent on $E_{pi}$ near the absorption edge, because [27],

$$f'(E_{pi}) + if''(E_{pi}) = \sum_n \frac{(f|H'|n)\langle n|H'|i\rangle}{E_n - E_i - E_{pi} + i\Gamma} \delta(E_i - E_f)$$ (12)

where $|f\rangle$ is the final state, $|i\rangle$ the initial state, and $n$ refers to the intermediate excited state, $\Gamma$ is the inverse of the life-time of the state, and

$$H' = \frac{\hbar}{m} \sum_{\nu} \epsilon_{\nu} \cdot p_{\nu} e^{ikr}.$$ (13)

where $\epsilon$ is the polarization vector of the photon electric field. Thus if the excited state is not isotropic due to ferroelectric polarization, the orientation dependence of the directional bond is reflected to the polarization dependence of the anomalous dispersion. Thus the absorption, which is the imaginary part of the anomalous dispersion, $f''$, shows polarization dependence [28]. Now if a diffraction measurement is made with the polarized x-rays tuned near the absorption edge it should be possible to determine the correlation in electronic polarization as well as ionic polarization. Such an experiment is planned in the near future.

X-ray resonant inelastic scattering

In the x-ray inelastic scattering (XIS) experiment the energy of the scattered photon, $E_{ps}$, is different from $E_{pi}$, therefore, $E_{ps} - E_{pi} = E_i - E_f \neq 0$. The amplitude of the scattered wave is given by [27],

$$A(E_{pi}, E_{ps}) = \frac{\hbar}{m} \sum_n \left[ \frac{\langle f|p_{qs} \cdot \epsilon_s|n\rangle\langle n|p_{ps} \cdot \epsilon_i|i\rangle}{E_n - E_i - E_{pi} + i\Gamma} + \frac{\langle f|p_{qi} \cdot \epsilon_i|n\rangle\langle n|p_{qs} \cdot \epsilon_s|i\rangle}{E_n - E_i + E_{ps} + i\Gamma} \right]$$ (14)

where

$$p_q = \sum_{\nu} p_{\nu} e^{i\nu r}$$ (15)

and $p_{qs}$ and $p_{qi}$ are momenta, and $\epsilon_s$ and $\epsilon_i$ are polarization vector, of the incident and scattered photons, respectively. Thus the momentum of the final state, $q_{fs}$, is equal to $q_i + q_{pi} - q_{ps}$. Since the incident energy of x-rays is of the order of 10 keV, in order to obtain 10 meV resolution in inelastic scattering the energy resolution of $10^{-6}$ is required. Not only that it is difficult to attain such a high resolution, but the measured intensity will be low. For this reason x-ray inelastic scattering is becoming feasible only in recent days, due to advances in synchrotron radiation technology. By XIS it is
possible to determine the electronic structure in detail, just as the photoelectron spectroscopy (PES). Unlike PES, however, XIS is not surface sensitive, since the x-ray penetration depth is far greater than that of photoelectrons. In addition electron-phonon coupling can be studied by XIS. While neutron inelastic scattering measurements yield phonon dispersions much more readily, they do not provide direct information on electron-phonon coupling. In particular, if the phonons induce charge transfer, as in the case of charge transfer compounds such as ferroelectric oxides or superconducting cuprates [29], the oscillator strength in (14) is greatly enhanced by the charge transfer between cation and anion, and the phonon cross-section should be increased by that much. Since the core electrons move with the nuclei, the scattering due to core electrons provides the same information as neutron scattering. On the other hand, the valence electron contribution gives the information regarding the charge transfer. In regular scattering the core electron contribution dominates since they are more numerous. However, in the resonant condition near the absorption edge the valence electron contribution is greatly enhanced by the vanishing denominator in (14), and its effect should be more easily observed [27]. In these measurements characteristic mode-dependence and $q$-dependence will be observed for the transition metal oxides. The phonon modes that induce charge transfer are longitudinal optical (LO) modes involving transition metal and oxygen [29], and are expected to show strong resonance effects. For FE oxides the zone-center ($q = 0$) should show a strongest resonance effect, while for Mott-insulators and related compounds including superconducting cuprates strong response is expected at the zone edge ($q = \pi a$) [30,31].

**CONCLUSIONS**

In spite of the impressive successes of the electron theories to describe the quantum effect on ferroelectricity, in studying real, complex materials much insight is still gained by resorting to classical crystal chemical ideas. In this paper we point out that one of the critical concepts, implicit in the crystal chemical approach, is the atomic level stresses, which can also be calculated quantum-mechanically. It is strongly recommended that such calculations be done. Examples are presented in which these concepts elucidate complex behavior of the systems with competing interactions, such as relaxor ferroelectrics. In addition several new x-ray scattering experiments that directly probe the relevant electronic features are discussed.

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REFERENCES: