

FERROELECTRICITY IN THE $\text{ReBa}_2\text{Cu}_3\text{O}_{7-\delta}$ SUPERCONDUCTORS

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Several independent pieces of physical evidence lead us to propose that the recently discovered high-temperature superconductors transform to a ferroelectric state prior to the onset of superconductivity.

It is becoming increasingly evident [1] that the ferroelastic domain structure of the $\text{ReBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramics has a major impact upon the high-temperature superconductivity exhibited by this family of complex perovskite structure oxides. The superconducting transition temperature has been shown to decrease rapidly with decreasing orthorhombicity $b-a$, going to zero at $b=a$ [2,3]. Domain refinement has been observed [2] upon annealing $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ near 240 K, as has an enhancement of the superconducting transition temperature T_{sc} to above 150 K [4]. Scanning tunneling microscope studies [5] suggest that the high-current metallic conductance is confined to narrow bands 80 Å wide spaced some 1000 Å apart. Field ion microscopy also suggests that nanoscale layered conductive regions exist in the orthorhombic superconducting phase [6]. Horowitz, Barsch, and Krumhansl [7] have proposed that a coherent oscillation of the ferroelastic domain walls may contribute to the enhancement of T_{sc} , though the exact coupling mechanism between the charge carriers and the walls was not specified.

It is clear from the crystal symmetries which have been proposed [8] that the $\text{ReBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds should be improper ferroelastics in the Aizu [9] species 4/mmm Fmmm. In this Letter we report a number of indirect pieces of evidence which sug-

gest that at a low temperature, which is still above the superconducting transition temperature T_{sc} , the material undergoes a diffuse phase change to a relaxor-type ferroelectric state. Such a transition has already been suggested by Scott [10] based upon temperature dependence of the Raman scattering. In particular the appearance of a peak at 646 cm^{-1} at temperatures below 240 K in the yttrium compound ($\text{Re}=\text{Y}$) has been taken as indicating a transition from a non-polar mmm crystal symmetry to a polar mm2 symmetry. A hypothetical discussion of a possible relation between high-temperature superconductivity and "quasi-ferroelectricity" has also been given by Zhongjin Yang and co-workers [11].

Following a procedure similar to that used in ref. [10] we have examined the Raman spectra of $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ which has a superconducting transition $T_{sc}=93\text{ K}$ and observe a strong line at 643 cm^{-1} for temperatures below 100°C (fig. 1). The temperature dependence of this peak is shown in the inset in fig. 1. Over the range from 100 to 180°C , this peak reproducibly disappears on heating and reappears on cooling, suggesting a broad diffuse phase transition. Evidence that such a diffuse phase change to a polar state occurs in the bulk of the sample, is found in measurements of the thermal expansion,

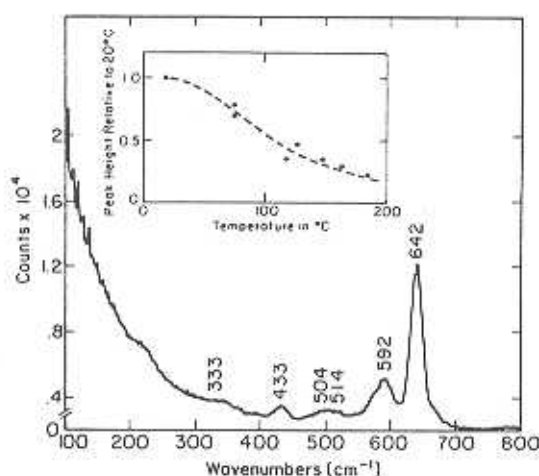


Fig. 1. Raman spectrum of optimum $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ sample ($T_c = 93 \text{ K}$, $\Delta T_c \approx 1 \text{ K}$, bulk resistance above $T_c \approx 1.5 \times 10^{-3} \Omega$) at room temperature. Exciting line 514.5 nm argon. Insert shows reversible temperature dependence of the 643 cm^{-1} peak in $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$. A similar temperature dependence was observed in several ceramic samples prepared from a different batch of starting powders. Stronger 643 cm^{-1} peaks appeared to be correlated with lower bulk resistance above T_c . A weaker peak at 630 cm^{-1} found in a pure BaCuO_2 ceramic exhibited similar temperature dependence when measured in the same Raman setup. No X-ray evidence was found for BaCuO_2 in the samples of $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Some samples, known to be superconducting, did not exhibit the strong peak at 643 cm^{-1} .

thermal lattice strain, and electrical resistivity which are shown in fig. 2.

If a polar phase of the ferroelectric relaxor type sets in below 180°C , then the rms polarization (P^2)^{1/2} must give rise to a lattice strain through the electrostriction effect, even though the electrical conductivity is very high. Assuming that the electrostriction constants are of similar magnitude to those of other perovskite relaxors, the strain data may be used to calculate an rms polarization of $0.1\text{--}0.15 \text{ C/m}^2$ at room temperature, as shown in fig. 2. This value is in reasonable accord with that to be expected from the Abrahams-Kurtz-Jamieson relations [12] for a perovskite oxide with a ferroelectric transition temperature T_c near 100°C and atomic displacements of 0.05 to 0.1 \AA .

Measurements [13] of the heat capacity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples shown in fig. 3 reveal a striking similarity to the recently measured [14] low-temperature heat capacity of the ferroelectric per-

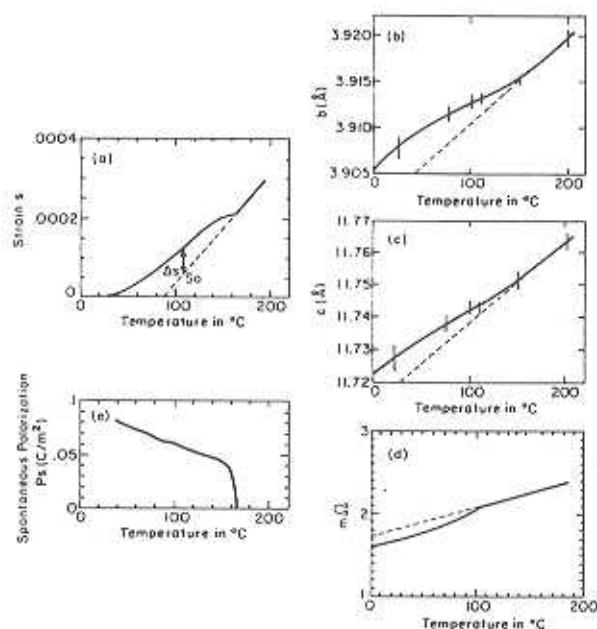


Fig. 2. Assorted experimental evidence of a diffuse phase transition to a polar state in $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in the range $100\text{--}180^\circ\text{C}$. (a) Thermal lattice expansion of bar-shaped sample. Deviations Δs from linear expansion S_0 are formed below $\approx 150^\circ\text{C}$. (b) and (c) Thermal lattice strain lattice constants b and c behave in similar fashion, suggesting that P_s is in the $\{011\}$ plane. (d) Electrical resistance from four-point probe measurement showing deviation from linear temperature dependence below 100°C . (e) Spontaneous polarization calculated from spontaneous strain data in (a) assuming electrostrictive coefficients identical to the relaxor PMN [22,23] (see text).

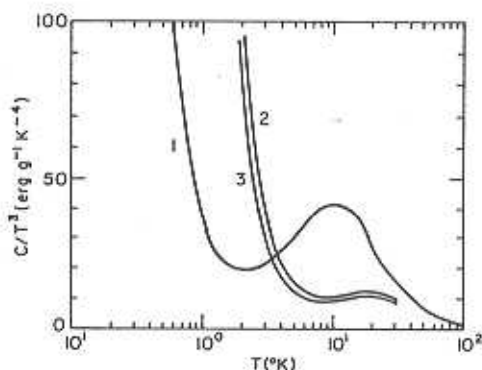


Fig. 3. Comparison of the temperature dependence of the specific heat of $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [12] with that of a known [13] ferroelectric relaxor $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$. The coexistence of Einstein and Schottky terms of this type has been found [13] to be characteristic of oxide perovskites being in a ferroelectric state.

ovskite relaxor $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$. One of us [15] has argued that this type of specific heat behavior, especially the Einstein peak in this temperature range, is a unique characteristic of a perovskite oxide when it is in a ferroelectric state. Anderson and Abrahams [16] have recently pointed out that the large discrepancies between the measured heat capacity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramics and the heat capacities expected from various theoretical models of high-temperature superconductivity may be a key to finding the correct physical mechanisms on which to base a theory.

Other features which have been reported that are suggestive of ferroelectricity in the $\text{ReBa}_2\text{Cu}_3\text{O}_{7-\delta}$ family include, anomalies in acoustic velocity and attenuation [17] and most recently the appearance of PTC-like [18] anomalies in the resistivity of partially reduced and re-oxidized $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ just at the 240 K Curie temperature [19]. Such PTC-like anomalies, which are well known in semiconducting BaTiO_3 , require the appearance of a spontaneous electrical polarization in order to reduce the barrier height between p-type grain boundary and n-type grain interior regions, thereby allowing strong conduction through the bulk ceramic just below the ferroelectric transition temperature. Changes in resistivity of seven orders of magnitude or more are routinely produced in this manner [20].

There is also accumulating evidence [1,21] that the low-frequency dielectric permittivity is in the range 800 to 3600 which is a nearly unique characteristic of an oxide ferroelectric. From group-theoretical arguments the only possible ferroelectric symmetries are $mm2$, m , and 1 , with $mm2$ the most probable [22]⁴¹. It must be stressed that in general relaxor ferroelectrics do not exhibit simple mode softening [24] and further that the customary X-ray and optical tests for the structural symmetry reductions which must accompany the onset of ferroelectricity are *not* usable [25]. This is in part a result of the very small (100 Å scale) size of the polar regions and their association with compositional heterogeneity).

⁴¹ More recent work [23] with convergent-beam electron microscopy has found some regions $mm2$ and some mmm (centrosymmetric and non-polar), consistent with the present relaxor hypothesis.

In view of the suggestion by Ginsburg [26] that a limited appearance of local negative permittivity is essential for an excitonic model of the high- T_c superconductor, and his invocation of the simple Clausius-Mössotti Lorentz-Lorenz formalism as a hypothetical example, the occurrence of ferroelectricity in the $\text{ReBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds could be of seminal importance to an excitonic mechanism of superconductivity. It is evident as shown in fig. 4 that in a ferroelectric below the Curie point T_c , if the single-domain polarization [27] is forced homogeneously to a low value, a regime of negative permittivity must appear. One may speculate that the origin of the suppression in the case of $\text{ReBa}_2\text{Cu}_3\text{O}_{7-\delta}$ oxide superconductors could be related to the peculiar nature of the domain structure, or in the compositional heterogeneity which gives rise to the relaxor character.

In conclusion, it must be stressed that further rigorous verification of ferroelectricity in these highly conducting systems will be a most difficult experimental task. Most evidence must be essentially indirect. For relaxor ferroelectrics the task is further complicated by the absence of a soft mode and the very small scale of the polar nanostructure (i.e. ≈ 100 Å). Even so, we believe that the general balance of evidence strongly suggests ferroelectricity and warrants serious exploration. Verification of ferroelectricity would have important consequences for future

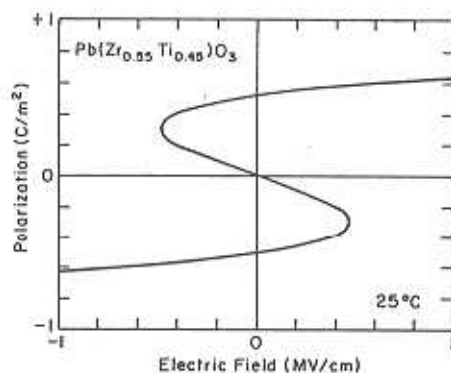


Fig. 4. Calculated [27] polarization versus electric field curve for ferroelectric lead zirconate $\text{PbZr}_{0.55}\text{Ti}_{0.45}\text{O}_3$ at room temperature. Clearly, if the homogeneous electric polarization is forced to a low value, a region of effective negative permittivity appears, and an attractive force between like charges of the type postulated by Ginsburg [26] will result.

success in the applications of high-temperature superconductivity ceramics.

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