

From one point of view this simple technique uses the additives as "indicators" to provide a new means for studying crystal growth. From another, it provides a new way to study molecular recognition by showing whether the growth site on a crystal surface can distinguish certain structural features of the additive. For example, a particular surface was shown to distinguish chlorine from iodine, but not from bromine.

If symmetry lowering in solid solutions is so general, it seems surprising that it was not recognized long ago, particularly in optical mineralogy, where solid solutions have been studied so extensively. Over the years anomalies have indeed been noted in which high symmetry minerals show division into sectors with lowered symmetry, but this phenomenon was usually attributed to strain fields or gross chemical segregation. By careful optical and X-ray studies Allen and Buseck recently established that sectoring in optically anisotropic grossular garnets is due to differing ratios of Al^{3+} to Fe^{3+} in octahedral sites which are nominally related by symmetry.^[4] To explain this desymmetrization they independently postulated the type of selection during crystal growth that was proposed by Lahav, Leiserowitz, and their collaborators.

For all its aesthetic appeal, crystal symmetry can become a liability for designing new materials, e.g. for nonlinear optics, when it results in cancellation of desired properties between symmetry-related molecules. The generality of symmetry lowering during crystallization of solid solutions provides a promising new approach for circumventing this obstacle.

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Ferroelectricity and Superconductivity

Some time ago the editor of this journal asked one of us (H. B.) to give, every now and then, comments on recent research news, of course, mainly concerned with materials science. Since most of the materials described in this journal are by far too complicated for basic theoretical investigations I wondered, being a theoretical physicist, what the editors really want to see in my comments. I decided that they probably want to have some founded speculations, some educated guesses, and perhaps a personal view on basic problems and ideas. Here is a first try; it is written under the impression that progress in modern materials science is mainly achieved under a broad view of various mechanical, electromagnetic or thermal properties of complex materials.

As an example, I want to discuss some theoretical considerations of the relationship between ferroelectricity and high-temperature superconductivity. This first comment is somewhat courageous as up to now there are many open questions since the pioneering ideas of B. T. Matthias^[1] who suggested that there must be a mutual exclusion of these two properties. I don't want to give a full account of the historical aspects of the following discussion but would like to point to another paper discussing the coexis-

tence of both effects.^[2] (Experimentally, for example, it is very difficult to measure a reversible polarization in good conductors, but it seems to have been established that the superconductor GeTe is also ferroelectric.) Today we know that ferroelectricity is inherently related to the local electron-phonon coupling resulting in a soft-mode behavior for displacive ferroelectrics.^[3] In recent years the late H. Bilz and his coworkers suggested a shell-model description of the lattice-dynamics of ferroelectrics where the main nonlinearity is locally centered at the lattice site of the chalcogen-ion (preferably oxygen) of representative ferroelectric materials.^[4] The microscopic origin of the lattice instability is the nonlinear polarizability of the electron cloud around the oxygen ion, resulting in a dynamic hybridization of the corresponding p-orbitals with the orbitals of the metal-ion ("dynamic covalency").

Recently (but before the discovery of the new high-temperature superconductors), discussion of a possible connection of both phenomena was taken up again. Within the shell-model the point was stressed that a dynamic covalency induces phonon anomalies.^[5] That might be thought of as the origin of both, ferroelectricity and superconductivity. Contrary to this, it was argued that pure static polar-

izabilities or static hybridizations are not favorable for these anomalies.

The spectacular discovery by J. G. Bednorz and K. A. Müller^[6] of the perovskite $\text{La}_{2-x}\text{BaCuO}_4$ as a high-temperature superconductor opens up again the discussion of the relationship between ferroelectricity and superconductivity. These materials and the later ones with even higher transition temperatures (the Y-Ba-Cu-O compounds as well as the Bi-Sr-Ca-Cu-O materials), not only show structural instabilities but are also structurally closely related to many ferroelectric oxides.^[7] There is even a ferroelectric-like instability in the Y-Ba-Cu-O compound at high temperatures inferred experimentally from a large dielectric constant.^[8] Here it should be pointed out that in spite of the structural similarity of both compounds additional doping and other defects destroy ferroelectricity, but simultaneously are necessary ingredients for superconductivity. This may yield some kind of material recipe to construct both kinds of properties. (Obviously K. A. Müller is by no accident also a highly respected expert in the fields of ferroelectric materials and structural phase transitions.)

In this new class of materials one should also consider the Ba-K(Pb)-Bi-O compound^[9] where Bi plays the role of the copper ion, not only allowing for a dynamic polarization of the oxygen but also giving rise to charge fluctuations at the metal site. All these facts are discussed in detail elsewhere^[10] where the original shell-model is extended and compared to other models. This point of view has now been taken up by several groups and becomes more and more popular. Recently it was shown^[11] that in the classical strong coupling formalism an increase in the transition temperature might occur if there is an anharmonic double-well interatomic potential. Such anharmonicities simultaneously, of course, must lead to lattice instabilities and its origin might be the dynamic covalency discussed above. In an interesting paper, Villars et al.^[12] systematically looked for chemical trends in both high-temperature superconducting materials and high-temperature ferroelectrics. They showed that three relevant parameters, namely the averaged valence electron number, the orbital radii of the ions and the electronegativity, determine the characteristic properties of both classes of materials. All these results together indicate the possibility of a common origin of both phenomena. While in ferroelectrics the instability of the oxygen ion triggers the high macroscopic polarizability, in superconductors we deal with a metal-ion with variable valencies. This discussion, mainly originating from a lattice-dynamical point of view, can also be carried out in the context of systems with correlated electrons. In this respect, Callaway et al.^[13] introduced their polarization induced pairing model. In an extended Hubbard system they calculated a phase diagram where, for reasonable interaction parameters, the possibility of electron pairing exists (whether this gives rise to long-range order superconductivity is still an open question). Quite recently Varma^[14]

studied a similar effect for the superconducting state resulting from an effective negative intra-atomic electron-electron interaction (especially for the Bi-ion). The origin of this negative interaction is an electron-transfer from the oxygen to the Bi-ion together with sp-hybridization. The same line of thought can be attributed to a paper by Tesanovic et al.^[15] in which a "unified" picture of the high-temperature superconductors is presented and, in addition to the above ideas, the importance of the various anisotropic geometries of the Cu(Bi)-O arrangements are discussed in detail. With these arguments we are back at the starting point where a mutual exclusion of ferroelectricity and superconductivity was supposed to be based upon geometrical reasons. Probably it is this anisotropy which favors high-temperature superconductivity, as it is also most important for ferroelectricity.

What do we learn from this interpretation of a common origin of ferroelectricity and high-temperature superconductivity? In both cases there is the possibility of a structural instability and therefore it might be worthwhile to look for noncrystalline, that is glassy or even fractal structures^[16], to further enhance the transition temperature. Furthermore, the proper choice of highly polarizable anions and valence fluctuating cations with the proper orbitals for hybridization may point to classes of other superconductors. But be cautious, this is a comment on some theoretical ideas of ferroelectricity and superconductivity. Nature might be more elegant.

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