SYMMETRY CONSIDERATIONS ON MARTENSITIC TRANSFORMATIONS: "FERROELECTRIC" METALS?

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The purpose of this Letter is to show that, according to Landau's general theory of phase transitions, second-order transitions usually involve some change in internal symmetry other than mere strain. The usual martensitic transitions are first order and may, and probably do, involve only strain, but if the recently discovered V_3Si transitions are second order, they must have some other motivation. We will suggest that these and perhaps several other metallic transitions may be "ferroelectric" in the sense of the appearance of a polar axis, or possibly at least involve the loss of a center of symmetry.

Batterman and Barrett[1] have demonstrated that V_3Si, and several other β-W structure superconductors, undergo transformations from cubic to tetragonal structures at temperatures T_m in the range immediately above their superconducting transition temperatures T_c. The authors describe these as "martensitic" transitions in the sense that no diffusion is involved; that is valid, of course, but the resemblance to the martensite transformation itself and to most others normally described as "martensitic" stops there. The V_3Si transformations appear typically second-order in that they go to completion at T_m and in that the accompanying deformation is slight and grows with $T_m - T$; this, the crystallography, the accompanying domain structure, and the specific heat[2] resemble those in a typical high-low, antiferroelectric, or ferroelectric transition like those of $BaTiO_3$ or $PbZrO_3$. Contrastingly, most of the canonical martensitic transitions are strongly first-order. There is, as reference 1 points out, at least one other case, that of In-Tl alloys, which is similar to V_3Si; in that case also the striking crystallographic resemblance to $BaTiO_3$ was noted.[3]

Landau's general theory of second-order phase transitions[4] can be extended to include structural transitions, and can be used to show quite generally the following: A transition from cubic to tetragonal in which the only order parameter in Landau's sense is the unit cell shape, i.e., the strain, can be second-order only with probability zero. This may be shown as follows.

The basic idea is that we apply Landau's concept of order parameter to homogeneous strains. In general, as in the present case, strain lowers the symmetry, but we will find that even nonsymmetry-breaking strains such as pure compression fit into our theory.

The strain $\eta_1 = c/a - 1$ carrying cubic to tetragonal is one of two symmetry-equivalent strains

$$\eta_1 = 6^{-1/2}(2S_{zz} - S_{xx} - S_{yy}),$$

$$\eta_2 = (1/\sqrt{2})(S_{xx} - S_{yy}),$$

belonging to the twofold representation of the cubic point group. By symmetry, $\eta_1 = \eta_2 = 0$ is a stationary point of the free energy F, so we may expand F as

$$F(T, \eta_i) = A + \tfrac{1}{2}B(T)(\eta_1^2 + \eta_2^2) + \textstyle\sum_{ijk} C_{ijk}(T)\eta_i\eta_j\eta_k + \cdots. \quad (1)$$

Since $\eta_1 > 0$ and $\eta_1 < 0$ are obviously distinct states, there is no reason why $C_{111}(T)$ should vanish, in general. Landau points out that a possible second-order transition occurs only when $B(T)$ and $C_{ijk}(T)$ vanish simultaneously, since only then is $\eta_i = 0$ both a relative and absolute minimum for all $B \geq 0$. Since normally the only available parameter is T, $C = B = 0$ is infinitely improbable. On the other hand, in many cases C or the equivalent quantity vanishes by symmetry. That is not so here, since we can exhibit the appropriate third-order term as

$$\tfrac{1}{4}C(T)(\eta_1^2 - 3\eta_2^2)\eta_1 = C(T)[S_{xx} - \tfrac{1}{2}(S_{xx} + S_{yy})] \times [S_{xx} - \tfrac{1}{2}(S_{yy} + S_{zz})][\cdots].$$

Landau's general group-theoretical criterion that $C(T)$ not vanish depends on whether a third-order invariant can be made up of the possible order parameters or not. If not, C in the general sense must be zero, and second-order transitions are possible. Pure strain transitions can be of one of three kinds:

(I). The first is those in which the symmetry does not change at all, for instance pure

volume transitions such as liquid-gas or the Ce transition. These are first order in general, though both examples given have critical points in P, T where they are second-order. For all of these the representation to which the strain belongs is the identity, and the cube of the strain is a point-group invariant.

(II). There is a relatively small set in which the symmetry changes and C vanishes by symmetry. Most of these are one-dimensional nonidentity representations for which the theorem is quite simple, e.g., tetragonal to orthorhombic, since the two orthogonal shears of a square are each other's negatives but also symmetry-equivalent, but at least one[5]—the axis-tilting shear in hexagonal symmetry—is higher dimensional.

(III). The third and most usual set involves any symmetry change in the cubic and trigonal classes and many in the hexagonal. In all of these cases there is a multidimensional representation to which the strain belongs, at least one possible strain of which is inequivalent to its negative. We find by an argument to be published elsewhere[5] that in all these cases, as in the cubic-tetragonal one, a third-order invariant can be found and second-order transitions are impossible.

From now on we shall talk entirely about the last set, to which belong all the transitions under discussion [and indeed, most martensitic transitions, most of the remainder being of the (I) kind].

For these kinds this result may be rephrased as follows: If the internal symmetry of the material does not change except as implied by the macroscopic strain it undergoes, the transition is necessarily first-order. Usually, in fact, martensitic transitions are quite thoroughly first-order; there are large hysteresis effects, large heat effects, and the change in structure is by a very considerable amount. We propose that it would be convenient to limit the use of the word "martensitic" to such transitions, which probably are motivated only by instability with respect to a finite strain.

It is interesting that most strain instabilities show up, therefore, as first-order transitions. Thus, the phonon velocity in a crystal is not only ≥ 0, but actually >0 by a finite, fairly large amount. This is worth noting since the positiveness of the sound velocity is a limitation on the permissible size of the electron-phonon interaction.[6]

Conversely, any observed second-order transition of this kind must have an internal symmetry change in addition to the change in lattice size and shape. We are familiar with this in many examples: magnetism, superconductivity, ferroelectricity, order-disorder, and "antiferroelectricity," and other superstructure effects. This seems to be true even in many transitions which are only approximately second-order, like $BaTiO_3$; in that and perhaps many other cases a change in the conditions ("clamping") makes the transition truly second-order.[7] The Batterman-Barrett transitions, then, if they are indeed second-order, must have some additional, as yet unknown, order parameters. No superstructure has yet been found, and no magnetic anomaly occurs. We are left with two possibilities: (1) some electronic mystery parameter, associated perhaps with pairing; or (2) some change in symmetry, such as the loss of the inversion center, which cannot easily be observed with x rays.

Certain facts other than simplicity favor this last possibility, or even the possibility of development of a polar axis, i.e., a transition structurally equivalent to ferroelectricity. First, this is equivalent to having a very low and temperature-dependent optical phonon branch,[8] which would favor superconductivity and lead to unusual temperature effects, such as are observed in these crystals. Second, while free electrons screen out the E field completely, they do not interact very strongly with the transverse optical phonons and the Lorentz local fields $F = LP$ which lead to ferroelectricity, since umklapp processes are forbidden as $k \to 0$. Thus, even the motivation might be electrostatic as in true ferroelectricity.

One other case which appears perhaps even more likely to be a ferroelectric metal is sodium tungsten bronze, as suggested to us by B. T. Matthias. The case of InTl remains a question. Here some data[3] suggest a first-order transition, but again not very much so. "Ferroelectricity" is out of the question, since all sites are equivalent in the fcc structure. Nonetheless, it seems not unlikely that in this material—and therefore also in In itself, according to the accepted phase diagram—the symmetry of the low phase may not be face-centered tetragonal but a less symmetric structure, such as might result, for example, if all the cube corner atoms were displaced a small distance δz and those on the faces parallel to

z a distance $\pm\delta z$. One of these examples retains a center of symmetry, but the other does not; they result if the longitudinal or transverse phonon at the zone boundary point in the 100 direction goes unstable. It is worth noting that there is a peak in superconducting transition temperature near the Tl concentration (~30%) at which this transition occurs near 0°K. This reinforces the notion that it is second-order.

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[1]B. W. Batterman and C. S. Barrett, Phys. Rev. Letters 13, 390 (1964).

[2]J. P. Maita and E. J. Ryder, private communication.

[3]L. Guttman, Trans. AIME 188, 1472 (1950).

[4]L. D. Landau and E. M. Lifshitz, Statistical Physics (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), Chap. XIV. This theory is at present considered to be incorrect in detail at the precise transition point, but the basic symmetry considerations do not seem to depend on the small singular terms which destroy the validity of the expansion (1) when $T \to T_c$, $\eta \to 0$. In particular, we believe our physical argument for $\eta = (c/a) - 1$ to be obviously valid with a greater degree of rigor than the expansion.

[5]These statements can be supported by a group theoretical demonstration. This and a complete classification of the various possible symmetry transformations will be published shortly.

[6]See, for example, W. Kohn and Vachaspati, Phys. Rev. 83, 462 (1951).

[7]A. F. Devonshire, Phil. Mag. 60, 1040 (1949); 62, 1065 (1951). This effect is the result of the coupling of internal symmetry to strain, which often adds a negative effective fourth-order term to Eq. (1). This strain effect can also be discussed more fully.[5]

[8]P. W. Anderson, Proceedings of the All-Union Conference on the Physics of Dielectrics of the Academy of Sciences of the U.S.S.R., December 1958, p. 290. W. Cochran, Phys. Rev. Letters 3, 412 (1959); Advan. Phys. 9 387 (1960).

[9]J. W. Stout and L. Guttman, Phys. Rev. 88, 703, 713 (1952).

PHOTOEMISSIVE DETERMINATION OF BARRIER SHAPE IN TUNNEL JUNCTIONS

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Tunnel junctions have been characterized in terms of three parameters, the barrier heights φ_1 and φ_2 and the width S, which generally are determined by a fit of experimental current-voltage characteristic curves with theory. In metal-semiconductor systems barrier heights have been determined independently of other parameters from measurement of the spectral dependence of photoresponse.[1,2] We wish to report the first results of the application of this technique to the measurement of the barrier heights in Al-Al_2O_3-Al and Al-Al_2O_3-Au tunnel junctions where the Al_2O_3 thickness is in the range of 20 to 40 Å.

The sample structures were fabricated by evaporating aluminum strips onto glass microscope-slide substrates at a vacuum of 10^{-6} Torr. The surface of these strips was oxidized in an oxygen glow discharge,[3] and the structure was completed by evaporation of a thin semitransparent counterelectrode of aluminum or gold. All 15 samples on a given slide showed uniformity of J-V characteristics and photoemissive properties. The data reported here are for a typical sample.

Al-Al_2O_3-Al tunnel junctions are observed to display asymmetric J-V characteristics, from which it is inferred that an intrinsic field exists in the Al_2O_3. Therefore, the experimental photoresponse must be analyzed on the basis of a trapezoidal barrier model such as is shown in the inset in Fig. 1(a). Two basic types of photoprocesses are possible. For photon energies $h\nu < \varphi_1$ the excited electrons can only tunnel through the barrier. For higher photon energies electrons can also be injected into the conduction band of the oxide over the barriers. In the latter case we assume that hot electrons lose their energy to the lattice in a distance small compared to the thickness of the oxide.[4] Hence electrons traveling against the electric field do not contribute to the pho-