

Letters to the Editor

Mean field models for martensitic and cooperative Jahn–Teller transformations

Abstract. The validity of mean field models for phase transitions is discussed, and examples are given for dilute random systems of anisotropic defects interacting with long range elastic strain fields. The distribution of internal fields, and not merely the moments, is calculated.

Isolated defects in cubic crystals may have point symmetry lower than cubic. We discuss cooperative phenomena in crystals containing a dilute random solution of such defects interacting through their long range elastic strain fields. There are thus substantial differences from the case of concentrated systems, where short range interactions dominate (Goodenough 1963, Wojtowicz 1959, Kanamori 1960, Sarfatt and Stoneham 1967, Novak 1969, 1970 a, b). In particular we discuss the distribution of the internal fields tending to cause cooperative alignment, and the specific application of a mean field theory to the cubic to tetragonal transition. The theory provides a model for some martensitic and cooperative Jahn–Teller transitions in a form which is free from arbitrary parameters.

To be specific, we assume the defects can be represented by x , y , or z force dipoles. Dynamical correlations are ignored, so we use an instantaneous, rather than retarded, interaction. Both this feature and the assumption that only discrete orientations are possible are good approximations in many cases; for the Jahn–Teller effect it means that we consider the static, rather than the dynamic, limit. In continuum elasticity the interaction of a defect at $\mathbf{r} = 0$ in orientation i with one in orientation j at $\mathbf{r} = \mathbf{R}$ can be written at large distances as

$$E_{ij}(\mathbf{R}) = \frac{M\psi_{ij}(X, Y, Z)}{R^3} \quad (1)$$

where X , Y , Z are the direction cosines of the position vector \mathbf{R} and $R \equiv |\mathbf{R}|$. The coefficient M can be determined either from the properties of the isolated defect or by a measure of the cooperative distortion (Zener 1948). Here we relate M to the Jahn–Teller energy, Δ , of an isolated ion by calculating both M and Δ for a model system of force dipoles. If the force dipole at $\mathbf{r} = 0$ consists of two antiparallel equal forces of magnitude $F^{(i)}$ a distance $2a^{(i)}$ apart and that at $\mathbf{r} = \mathbf{R}$ consists of two analogous forces $F^{(j)}$ a distance $2a^{(j)}$ apart then M has the explicit form

$$M = \frac{F^{(i)}F^{(j)}a^{(i)}a^{(j)}}{4\pi\mu(1-\nu)} \quad (2)$$

where repeated indices are *not* summed, μ is the shear modulus and ν is Poisson's ratio. The ψ_{ij} are given by

$$\begin{aligned}\psi_{zz} &= 15Z^4 - 6Z^2 - 1 + 4\nu(1 - 3Z^2) \\ \psi_{xz} &= 15X^2Z^2 - 3X^2 - 3Z^2 + 1\end{aligned}\quad (3)$$

other ψ_{ij} can be found by symmetry.

We now calculate the distribution of ϵ_{ik} , the difference in energy for a defect in the i and k orientations, using the 'statistical method' (Stoneham 1969 reviews this approach). The method assumes that ϵ_{ik} is simply the sum of terms from each of the other defects in the crystal and that the distribution of defects in space and in orientation may be expressed in terms of a pair distribution function $p(\mathbf{R}, j)$. A low concentration assumption is implicit since only one defect should occupy each site. If $\epsilon_{ik}(\mathbf{R}, j) \equiv E_{ij}(\mathbf{R}) - E_{kj}(\mathbf{R})$ and ρ is the total density of defects per unit volume, then the distribution of ϵ_{ik} is

$$I(\epsilon_{ik}) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(ix\epsilon_{ik} - \rho J(x)) dx \quad (4)$$

$$J(x) = \sum_j \int d^3\mathbf{R} p(\mathbf{R}, j) \{1 - \exp(-ix\epsilon_{ik}(\mathbf{R}, j))\} \quad (5)$$

These results simplify enormously if we assume that $p(\mathbf{R}, j) = f_j$, the fraction of defects in state j . The degree of alignment along, say, the z axis is measured by $(f_z - \frac{1}{3}) \equiv f$, and we may compute the distribution I_{xz} as a function of f . These results are directly relevant to the mean field theory. Specifically, I_{xz} is Lorentzian [$I \simeq \{\delta^2 + (\epsilon - \bar{\epsilon})^2\}^{-1}$] in our approximations, with a width

$$\begin{aligned}2\delta &= M\rho \left\{ \left(\frac{2}{3} + f\right) \frac{\pi}{6} \int_{4\pi} d\Omega |(\psi_{xz} - \psi_{zz})| + \left(\frac{2}{3} - f\right) \frac{\pi}{6} \int_{4\pi} d\Omega |(\psi_{xy} - \psi_{zy})| \right\} \\ &= M\rho (19.193 - 0.047f)\end{aligned}\quad (6)$$

and a shift, which gives the mean field

$$\begin{aligned}\bar{\epsilon} &= fM\rho \left\{ -\frac{1}{2} \int_{4\pi} d\Omega (\psi_{xz} - \psi_{zz}) \ln |(\psi_{xz} - \psi_{zz})| \right\} \\ &= +3.717 \rho Mf\end{aligned}\quad (7)$$

in which we use $\nu = \frac{1}{3}$. It is clear that the fluctuations in the internal field are always much larger than the mean field, even when there is a high degree of alignment ($f \simeq \frac{2}{3}$).

For completeness we summarize the result of a mean field calculation, despite the limitations of its validity. We find that (a), the transition occurs at a temperature $kT_c = 0.9026 \rho M$, linear in M and in the defect concentration, and that (b), a latent heat $0.234 \rho M$ per defect, so that this is a first order transition in which f changes discontinuously in the transition. The defect 'strength' parameter M can be related to Δ , the Jahn-Teller energy per defect, in appropriate cases. If a is the nearest neighbour distance then $M = \frac{1}{16} \Delta a^3 / (1 - \nu)$. In other cases, other definitions of M are appropriate. Thus Zener (1948) related the critical temperature to the difference between the instantaneous and static compliances of the system. To give orders of magnitude, if $\Delta \simeq 1$ eV, $\nu = \frac{1}{3}$, $a = 2$ Å and a fraction 10^{-2} of sites are occupied then $T_c \simeq 10$ K, and the latent heat $\simeq 4 \cdot 10^5$ erg cm $^{-3}$. However, in view of the doubts about mean field theory, these results should be regarded with caution. Cooperative behaviour has been seen for electric dipoles in similar circumstances by Fiory (1969). However it is by no means clear,

either experimentally or from the preliminary calculations we have made, which attempt to include the fluctuations, that there is a sharp ordering transition in such dilute systems.

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1st October 1970

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Axial ratios of hexagonal metals

Abstract. Calculations of the equilibrium axial ratios of beryllium, magnesium, zinc and cadmium based on the optimized model potential are compared. The condition for a large axial ratio is examined. A recent empirically determined change in the normalized energy–wavenumber characteristic in the structure region for zinc and cadmium helps to satisfy this condition and consequently improves the axial ratio prediction.

This note is an addendum to a recent paper describing the calculation of the second order elastic shear constants of four hexagonal close-packed metals (Cousins 1970). The calculations were based on the normalized energy–wavenumber characteristic $G(y)$, where $y = q/k_F$, of the optimized model potential (Shaw 1969, Shaw and Pynn 1969) and were successful for beryllium and magnesium but very poor for zinc and cadmium. It proved possible, nevertheless, to invert the shear constant data to produce an empirical $G(y)$ valid in the structure region, which would accurately predict the shear constants. As expected the modifications were small for beryllium and magnesium, whilst those for zinc and cadmium were similar to each other and were limited to the vicinity of only the $\langle 10\cdot1 \rangle$ set of the three sets of reduced reciprocal lattice vectors that dominate the band structure contributions to the shear constants.

Using the same model the structure dependent energy, $U_s = U_{ES} + U_{BS}$, has been calculated as a function of $\gamma (= c/a)$ at the observed atomic volume. Again only the first three sets of vectors in reciprocal space were considered for the band structure part, U_{BS} , since these lie in the region where the slope of $G(y)$ is greatest and are sufficient for locating the minimum. U_{BS} is never more than 3% of U_{ES} , the electrostatic part, yet it varies sufficiently strongly with γ to move the resultant minimum of U_s away from $\gamma = 1.636$, where U_{ES} is minimized (Cousins 1968). The results are given in table 1. NXC is Shaw's calculation when $G(y)$ is computed in Hartree approximation, XC is based on the Shaw–Pynn calculation with correction for exchange and correlation and M is based on the empirical modification to $G(y)$ mentioned above. Except for magnesium where the agreement with observation