

Possibility of Jahn-Teller glass formation

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Jahn-Teller ions in crystals exert forces on their neighbors and are, thereby, indirectly coupled by Ising-type interactions. By a simple physical argument it is shown that the sign of the interaction can be positive or negative, depending on the relative positions of the ion pairs. This is the condition for Jahn-Teller glass formation in randomly doped crystals. At low enough temperatures, the lattice would be randomly statically strained.

The tetragonal rare-earth zircons, with D_{4h}^{19} space symmetry, have been of interest over the past decade because of their ideal suitability for the study of the cooperative Jahn-Teller (JT) effect.¹⁻³ More recently, it has been shown that the degeneracies, which the JT phase transition resolves in a cooperative way are, in fact, already resolved in a random way above the phase-transition temperature.⁴ That this is likely can be seen by applying the displaced oscillator transformation¹ to the effective Hamiltonian which is usually introduced to describe the cooperative JT effect,

$$\mathcal{H} = \sum_k \hbar\omega(\vec{k})(\alpha_k^\dagger \alpha_k + \frac{1}{2}) + \sum_{k,n} \exp(i\vec{k}\cdot\vec{R}_n) \xi(\vec{k}) S_z^n (\alpha_k + \alpha_{-k}^\dagger), \quad (1)$$

where the two terms refer, respectively, to the phonons and their interactions with the JT ions represented by pseudospins S^n . After the transformation, the equivalent Hamiltonian is

$$\tilde{\mathcal{H}} = \sum_k \hbar\omega(\vec{k})(\gamma_k^\dagger \gamma_k + \frac{1}{2}) - \sum_{n,m} J_{nm} S_z^n S_z^m, \quad (2)$$

where

$$J_{nm} = \sum_k \frac{|\xi(\vec{k})|^2}{\hbar\omega(\vec{k})} \exp[i\vec{k}\cdot(\vec{R}_n - \vec{R}_m)] \quad (3)$$

which shows that the pseudospin-phonon interaction [the second term in Eq. (1)] can be replaced by an Ising-type interaction between the pseudospins [the second term in Eq. (2)]. Each pseudospin can thus be regarded as being in a local field due to the other pseudospins. (It should, however, be noted that the argument is not entirely satisfactory because the starting Hamiltonian \mathcal{H} does not include all terms which will be present in an actual system. In partic-

ular, there are no terms which lead to pseudospin flips.) The resolution of the degeneracies in the high-temperature phases of TmVO_4 and TmAsO_4 has been confirmed by experiment.⁴⁻⁶

In a fully concentrated crystal there is a transition, at low enough temperatures, to a cooperative phase which, usually, is the analog of a ferromagnetic transition. The processes which induce pseudospin flips then become relatively unimportant and each pseudospin has a definite direction of alignment, all alignments being the same for a ferrodistorptive phase. The phase change is then recognized because the crystal structure is altered.

In view of the present interest in spin-⁷ and other⁸⁻¹¹ glasses, the question arises as to whether a diluted JT system will show a JT glass phase. As the JT-induced strains are triggered by initial electronic degeneracies, the JT glasses would closely resemble the ordinary spin-glasses which also arise from electronic degeneracies. It is already known that in a paradistorptive phase the pseudospin lifetimes are quite long,¹² but the essential requirement for a glass, that the effective Ising exchange interactions appear with both positive and negative signs,¹³ though indicated by the form of the interaction in Eq. (3), has not been convincingly demonstrated. If both signs do occur, then in a diluted system it is possible to envisage that at low enough temperatures each pseudospin will become aligned in a definite direction, but with some pseudospins directed along the positive z direction and others along the negative z direction. (These are not true spatial directions because pseudospins are being used. Rather, they correspond to local distortions of the lattice.) The main purpose of this paper is to present a simple argument, for a model system, which shows that both signs of interaction can be expected.

For simplicity we introduce, in Fig. 1, a two-dimensional square lattice of ions which are not themselves JT active but are simply to provide crys-

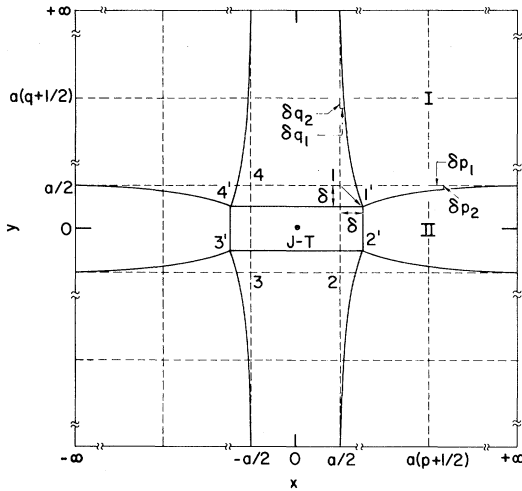


FIG. 1. Ideal infinite-square lattice distorted by a single Jahn-Teller ion at the origin.

tal fields of the required symmetry. They are taken to be at the positions $a(p + \frac{1}{2}, q + \frac{1}{2})$, where a is the lattice constant and p and q are integers. In general, the JT ions will be at positions $\vec{R}_m = a(p, q)$ but for the moment we assume that only one JT ion is present at the origin and the other sites are occupied by non-JT ions. The JT ion is, therefore, in a tetragonal crystal field, and we assume that its energy level pattern is such that the lowest energy is doubly degenerate, and described by a pseudospin $\frac{1}{2}$.

It is next supposed that the degeneracy can be removed by a B_{1g} distortion so that the immediate neighbors of the JT ion at the origin form a rectangle rather than a square. If the neighbors at the (p, q) positions $(0, 0)$, $(0, -1)$, $(-1, -1)$, and $(-1, 0)$ are denoted, respectively, by 1, 2, 3, 4, the JT coupling can be written as

$$\mathcal{H}_{JT} = -\lambda Q^0 S_z, \quad (4)$$

where

$$Q^0 = X_1^0 + X_2^0 - X_3^0 - X_4^0 - Y_1^0 + Y_2^0 + Y_3^0 - Y_4^0 \quad (5)$$

and (X_n^0, Y_n^0) denote the displacements of the n th neighbor ($n = 1, \dots, 4$) of the JT ion at the origin. Suppose first that the JT ion has $S_z = +\frac{1}{2}$. The physical interpretation of the interaction is that there are forces on the immediate neighbors and, therefore, on the lattice as a whole. It will, therefore, distort. Taking the nearest-neighbor displacements to be $(\delta, -\delta), (\delta, \delta), (-\delta, \delta), (-\delta, -\delta)$, so that the immediate neighborhood is rectangular, Q^0 becomes 8δ and the $S_z = \frac{1}{2}$ state has an energy change $-4\lambda\delta$. It is typical of JT systems that if the ion is

alternatively in $S_z = -\frac{1}{2}$, the sign of δ is reversed, the distortion is reversed, and its state is changed in energy by $-4\lambda\delta$, which is precisely that found for $S_z = +\frac{1}{2}$. Whichever state is chosen, the symmetry of the immediate neighbors will be rectangular and this symmetry will also be found for the lattice as a whole. However, a randomly chosen unit cell is unlikely to show this symmetry and in detail there is very little symmetry left. It is a remarkable result, a consequence of assuming that the lattice is harmonic, that the vibrational spectrum is unaltered.¹⁴ The vibrations do, of course, take place about the distorted lattice.

Now suppose that a second identical JT ion is used to probe the local distortions in the crystal, and that like the central ion it is only sensitive to the displacements of its neighbors which contribute to the local Q . That is, if the neighbors of the probe at point \vec{R}_m were also numbered from 1 to 4 as for the central ion, the probe would measure

$$Q^m = X_1^m + X_2^m - X_3^m - X_4^m - Y_1^m + Y_2^m + Y_3^m - Y_4^m. \quad (6)$$

The important question with regard to glass behavior is whether, as the probe moves through the crystal, it sees local Q 's of both signs, for a definite state of the central ion. (The distortion Q^m at \vec{R}_m is produced by the JT ion at the origin. Of course the probe ion will itself induce lattice strains, but as the strain fields in a harmonic crystal are additive, they are not relevant.) It is a difficult problem to determine the value of a local Q because it involves a knowledge of the lattice potential. Rather, it is much more convenient to determine the sum of the Q 's (produced by one JT ion at the origin) for some chosen region of the crystal. The important consideration here is that if a lattice-point interior to the region is considered, its displacement contributes to four Q 's because the point belongs to four unit cells. Further, its net contribution to the sum vanishes, as can be seen from the structure of Q . It follows that the only contribution to the sum over a given region comes from the lattice points on its boundaries.

Consider, therefore, the line $y = a/2$ in Fig. 1. With the strain present, the point $x = a/2$ on this line (point 1) has a displacement $(\delta, -\delta)$, where δ is positive. It can be expected that all lattice points on the line with positive x will have displacements in approximately the same direction, so that the displacement at $a(p + \frac{1}{2}, \frac{1}{2})$ can be taken to be $(\delta p_1, -\delta p_2)$ where δp_1 and δp_2 are both positive. Next, consider the line $x = a/2$. The displacement at $a(\frac{1}{2}, q + \frac{1}{2})$ can be expected to be $(\delta q_1, -\delta q_2)$ with δq_1 and δq_2 both positive. These two lines, to-

gether with a boundary at infinity divide the crystal into two regions. That for which p and q are positive will be called region I. Assuming that the points at infinity are fixed, the sum of all Q 's of all the cells in region I is just the sum of the contributions from the points on the two lines. For $p, q > 0$, the point $a(p + \frac{1}{2}, \frac{1}{2})$ makes a contribution $-2\delta p_2$, for it belongs to two cells in region I, in one of which it contributes like ion 2 of the central cell and in the other like ion 3. Similarly, the point $a(\frac{1}{2}, q + \frac{1}{2})$ contributes $-2\delta q_1$. There remains the point $a(\frac{1}{2}, \frac{1}{2})$ which belongs to only one cell. It contributes -2δ . Thus the total contribution from all the cells in region I is negative. A similar argument shows that the contribution from region II shown in Fig. 1 is positive. This result, that the sums of the Q 's in the two regions are of opposite signs, is enough to show that some local Q 's are positive and some are negative, so that conditions are right for obtaining effective Ising exchange interactions of both signs.

The argument is readily extended to a three dimensional lattice, by simply considering each lattice plane in turn. Another possibility is that the coupling to the JT ion depends on a B_{2g} distortion:

$$Q' = X_1 - X_2 - X_3 + X_4 + Y_1 + Y_2 - Y_3 - Y_4. \quad (7)$$

The same choice of regions shows that both signs will occur. Another point is that crystal fields depend on relative coordinates and perhaps the JT probe is not at the center of its cell. Denoting its position by (X_0, Y_0) it could be reasoned that $X_1 - X_0$, etc. should be used instead of X_1 , etc. It will be noticed that if this is done, Q does not involve X_0 and Y_0 , so the reasoning is unaffected. The weakest point in the argument comes if the

crystal being considered is such that the JT ion is coupled to neighbors which are within the unit cell, rather than on its boundaries. The cancellation for interior cells do not then occur, at least by the arguments presented. Nevertheless, it would be surprising if the local strains are not proportional to the unit cell strains when they would continue to cancel.

As far as is known, there is no experimental evidence for JT glasses—lattices with frozen-in random-strain fields due to the presence of JT ions. However, the prospect that they will exist looks promising for it is certainly possible to dilute JT crystals with non-JT ions. These diluents may also introduce strains, due to the size differences, which at the JT sites will appear as static contributions to the local Q values. It will be a requirement that they be much smaller in magnitude than the JT strain in the glass phase. Present evidence in fairly dilute crystals of $Tm_x Y_{1-x} VO_4$ is that this can be achieved.¹²

Another, though less attractive possibility, is to achieve the effect of random doping by thermal means. If the temperature is raised it is not uncommonly found that the excited states of the JT ions are singlets and so do not show JT couplings. A further possibility, along the same lines, comes as recent work¹⁵ has shown that in some cases it is possible to thermally populate higher levels, which do show JT couplings, even though the ground level is non-JT. This result has been obtained by studying the electron spin resonance spectra of Gd^{3+} impurities in $TmPO_4$.

We conclude that there is a strong probability that the analogs of Ising spin-glasses will be found with Jahn-Teller systems, and that, in them, frozen-in random strains, arising from the initial electronic degeneracies, will take the place of randomly aligned magnetic moments.

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