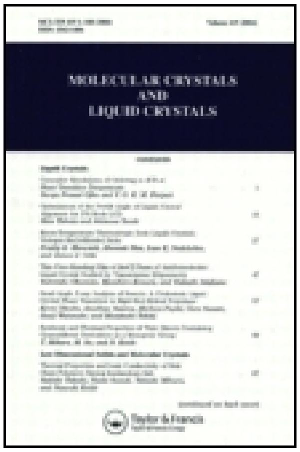

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Orientational Ordering in Solid N_2-Argon Mixtures: Collective versus Non-Collective Behavior†

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We compare the temperature variation of the local orientational order parameters and the Edwards-Anderson glass order parameter deduced from available NMR data, with the variations expected for a non-collective local random quadrupolar field model. The analysis of the experimenal results for solid N_2-Argon alloys indicates a weak collective behavior and new experiments are suggested to test for true glassy behavior.

I. INTRODUCTION

Experiments on dilute molecular systems such as solid ortho-/para hydrogen mixtures and nitrogen/argon mixtures have been carried out by a number of groups[1–15] in recent years. The interest in these systems is that they represent a random array of interacting quadrupoles which has an interesting analogy with the spin glasses. The essential feature is that while the centers of mass of the molecules are fixed at the sites of an hcp lattice, the molecules are free to rotate until cooled. At low temperatures the weak, highly anisotropic interactions, principally electric quadrupole-quadrupole, lead to an orientational ordering of the molecular axes. Of the two molecular species of hydrogen, only ortho-H_2 with angular momentum $J = 1$ is orientable. The para species ($J = 0$) being spherically symmetric plays the role of an almost perfect diluant. For nitrogen-argon alloys,

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the nitrogen molecules bear the quadrupole moments while the argon atoms serve as diluants.

If the quadrupolar concentrations are sufficiently high (greater than 55% for ortho-H_2 in ortho-para mixtures and 78% for N_2 in N_2-Argon), a periodic orientational order in a 4-sublattice Pa_3 configuration is obtained. The transition to the ordered phase is first order and triggers a lattice change to a f.c.c. structure. The long range ordered structure is highly frustrated. The minimum energy configuration for a pair is a "Tee" configuration and the nearest neighbors in the Pa_3 configuration are aligned parallel to different body diagonals of an f.c.c. lattice with an interaction energy only 0.53 that of the "Tee" alignment. Replacement of one of the quadrupoles by a spherically symmetric molecule leads to substantial rearrangement of its neighbors, and below the critical concentration the long range periodic order is lost.

In the low concentration regime, the molecules become frozen in random configurations with different orientations at different sites, and for this reason these systems have been referred to as orientational glasses.[2-3] There is no evidence of a well-defined transition from the high temperature para-orientational phase to the glass phase.[1,2,4] The crystal structure remains hcp down to very low temperatures[14,15] and this has a significant bearing on whether or not a clear transition could occur. For the hcp lattice, the effect of having a random occupation of lattice sites leads automatically to the existence of local electric field gradients, the field conjugate to the local order parameter, which plays the same role as the magnetic field for the dipolar spin glasses.[2] This random field therefore makes the problem of local orientational ordering in random mixtures equivalent to the local dipolar ordering in spin glasses in the presence of random internal fields and this may smear out the transition, or if sufficiently strong, prevent the occurrence of a transition.[1] In view of this uncertainty it is important to try to determine from the existing data, whether or not the temperature dependence of the local molecular order parameter shows any evidence of collective behavior. The purpose of this paper is to show that the reported experimental values for the growth of local orientational order for nitrogen-argon mixtures, given by the mean square alignment, has a much stronger temperature dependence than that expected for a "non-collective" independent particle random quadrupolar field model. The analysis suggests a smooth evolution with temperature over the 7–15 K range for which one also observes a linear dependence in the heat capacity[7,8] and a strong attenuation of the Raman scattering for 10–25 cm^{-1}.[16]

II. ORDER PARAMETERS

If the diatomic molecules have a preferred orientation, the local order parameters are given by the expectation values $\langle Q_{\alpha\beta}\rangle$ of the molecular quadrupole moment operators $Q_{\alpha\beta}$. The $Q_{\alpha\beta}$ are second rank tensorial operators and it is convenient to choose an irreducible set $Q^{(2)}_{mn}$, which transform in the same manner as the spherical harmonics $Y^{(2)}_{mn}$. Not all of the $\langle Q^{(2)}_{mn}\rangle$ are independent and only 5 independent parameters are needed to specify the orientational degrees of freedom, e.g., in terms of the density matrix operator[17]

$$\rho = \frac{1}{3}\Pi_3 + \sum_{m,n} \langle Q^{(2)}_{m,n}\rangle\, Q^{(2)+}_{m,n}$$

Π_3 is the unit operator.

Furthermore, if we choose local axes (x, y, z) which correspond to the principal axes for the quadrupole moment tensor $\overset{\rightrightarrows}{Q}$, only two independent parameters are needed. These parameters are[18]

(a) the mean *alignment* along the principal axis

$$\sigma_i = \sqrt{\frac{16\pi}{15}}\,\langle Y^{(2)}_{20}\,(\theta_i)\rangle$$

$$= \langle 3\cos^2\theta_i - 1\rangle$$

and (b) the average *eccentricity*

$$\eta = \sqrt{\frac{8\pi}{15}}\,\{\langle Y^{(2)}_{22}\,(\theta_i, \phi_i) + Y^{(2)}_{2,-2}\,(\theta_i, \phi_i)\rangle\}$$

$$= \langle x_i^2 - y_i^2\rangle .$$

i labels each molecule and (θ_i, ϕ_i) are the polar angles specifying the orientation of the molecular axis with respect to the local axes (x_i, y_i, z_i). The eccentricity is strictly speaking the eccentricity of the probability distribution for the molecular orientation when referred to the local axes. The above expressions are only valid for classical diatomic molecules such as N_2. For ortho hydrogen which is a quantum rotator with angular momentum $J = 1$, we must replace the above by their operator equivalents σ_q, η_q in the manifold $J = 1$. ($\sigma_q = \langle 3J_z^2 - J^2\rangle$

and $\eta_q = \langle J_x^2 - J_y^2 \rangle$.). In the presence of axial symmetry the η vanish at each site and in the long range ordered Pa_3 structure $\sigma_i = -2$ at each site.

The *new feature* of the glass phases is that the NMR experiments have been able to show that at low temperatures there is a broad distribution of both local axes and local order parameters.[5,12]

The great advantage of the experimental method employed is that the local order parameters can be observed directly by NMR techniques. The reason for this is that the intramolecular nuclear dipole-dipole interaction H_{DD_i} and the anisotropic chemical shifts H_{χ_i} (if any) depend directly on the local order parameters. The secular components of these interactions are

$$H^0_{DD_i} = -\frac{1}{3} D\, P_2(\theta_i)(3I^2_{Z_i} - I^2)$$

and

$$H^0_{\chi_i} = \chi_{ac} P_2(\theta_i) I_{Z_i}$$

respectively.

θ_i specifies the orientation of the ith molecule with respect to the applied magnetic field (Z axis). $P_2(\theta_i)$ is the Legendre Polynomial. D and χ_{ac} are constants representing the strengths of the dipolar interactions and the chemical shifts, respectively. If for a time scale $t > t_{\text{molecular}} \approx D^{-1}$ (or χ^{-1}) we can describe the molecular orientations by a probability distribution with principal axes (x_i, y_i, z_i) and order parameters (σ_i, η_i) as discussed above, then we can write

$$\langle P_2(\theta_i) \rangle = \sigma_i P_2(\gamma_i) + \frac{3}{4} \eta_i \sin^2\gamma_i \cos 2\tau_i$$

where the polar angles (γ_i, τ_i) give the orientation of the applied magnetic field with respect to the local molecular triad (x_i, y_i, z_i). The intramolecular dipolar interactions H^0_{DD} and chemical shifts H^0_{χ} are seen to depend directly on the order parameters (σ_i, η_i) and the angles (γ_i, τ_i). If the order parameters do not vanish the NMR line shapes acquire a fine structure which depends on the values of the order parameters. In the long range ordered phase $\sigma_i = -2$, $\eta_i = 0$ at each site and for a power sample (i.e., white distribution of solid angles $d\Omega_i = 2\pi \sin\gamma_i d\gamma_i d\tau_i$) one finds the familiar Pake doublet lineshape.[19] The NMR studies reported in Reference 12 used the rare isotope ^{15}N for which the intramolecular dipolar interactions and asymmetrical chemical shift are of comparable magnitude. The chemical shift leads to a distorted Pake doublet but the line shapes can still be interpreted in terms of an order parameter distribution. The reader is referred to References 12 and 18 for details. The separation of the cusps is directly proportional to σ. In the glass phase the line shapes are interpreted in terms of a broad distribution $P(\sigma)$ of order parameters (with $P(\sigma)$ approximately linearly dependent on σ at low quadrupole concentrations). In the analysis of the data all groups have made the assumption of local axial symmetry, i.e., that $\eta_i = 0$ to a good approximation at each site, although this has never been proved explicitly.

The NMR absorption lineshapes are therefore interpreted in terms of a probability distribution $P(\sigma)$ for the order parameters σ. For a given quadrupole concentration the lineshapes are carefully recorded (taking great care to observe the absorption and not a mixture of absorption and dispersion) for a range of temperatures covering the transition from the disordered phase to the low temperature phase where $P(\sigma)$ ceases to change with further cooling.

The significant feature of the magnetic spin glasses (spin 1/2, dipolar glasses) which distinguishes them from the completely disordered paramagnetic phase is the non-vanishing of the *Edwards-Anderson order parameter*[20]

$$q_{\mathrm{EA}}(T) = [\langle S_i \rangle_T^2]_C$$

S_i is the spin component at the ith site, $\langle\ \rangle_T$ designates a thermodynamic average and C refers to a configurational average over the sample. While $[\langle S_i \rangle_T]_C$ vanishes for both the spin glass phase and the paramagnetic phase, the Edward-Anderson parameter does not vanish for the spin-glass phase

$$q_{\mathrm{EA}}(T) \neq 0 \quad \text{spin glasses}$$

$$q_{\mathrm{EA}}(T) = 0 \quad \text{paramagnetism}\,.$$

For the quadrupolar glasses, the Edwards-Anderson parameter can be determined directly from the NMR data, as it is directly proportional to the second moment of $P(\sigma)$ which is simply the intramolecular component of M_2, the dipolar second moment of the NMR lineshape.[1]

$$M_2^{\text{intra}} = \frac{9}{5} D^2 q_{\text{EA}}(T) \quad \text{where for the quadrupolar glasses,}$$

$$q_{\text{EA}}(T) = \int \sigma^2 P_2(\sigma)$$

with $\sigma_i = \langle 3\cos^2\theta_i - 1 \rangle$

While the Edwards-Anderson parameter vanishes for the magnetic spin glasses, this is as pointed out by Esteve et al.[5] and Harris et al.[1,4] and indicated in the introduction, not true for the quadrupolar system.[2,4] The essential point is that the local symmetry is broken even in the completely disordered paraorientational phase by the replacement of a neighboring quadrupole by a spherical molecule. The order parameters resulting from this dilution effect alone can be calculated in the high temperature limit and is given by[2,4]

$$q = 3X(1 - X)(5\Gamma/3T)^4.$$

for a quadrupole concentration X.

This non-cooperative symmetry breaking would certainly tend to mask any clear transition to a quadrupolar glass phase and may even prevent any transition from occurring.[4] In the latter case, the glass order parameter $q_{\text{EA}}(T)$ would grow smoothly and slowly with temperature according to a random molecular field generated purely by the local dilution effects at any given site. The purpose of this paper is to compare the temperature dependence of the Edwards-Anderson parameters (as obtained from the NMR results) with the behavior of the parameter expected for a simple non-collective random molecular field model. We will also compare the experimental results with recent calculations of Kokshenev[21,22] who has used simplified spin glass models for the quadrupolar systems.

III. DISCUSSION OF EXPERIMENTAL RESULTS

The distribution functions $P(\sigma)$ for the order parameters obtained by Esteve et al.[12] for N_2-argon alloys ($X_{\text{quad.}} = 0.67$) is shown in Figure 1 for a set of temperatures spanning the transition region. The calculated second moments $M_2(T) = \langle \sigma^2 \rangle$ and mean values $M_1(T) = \langle \sigma \rangle$ are plotted as a function of temperature in Figure 2. As discussed in

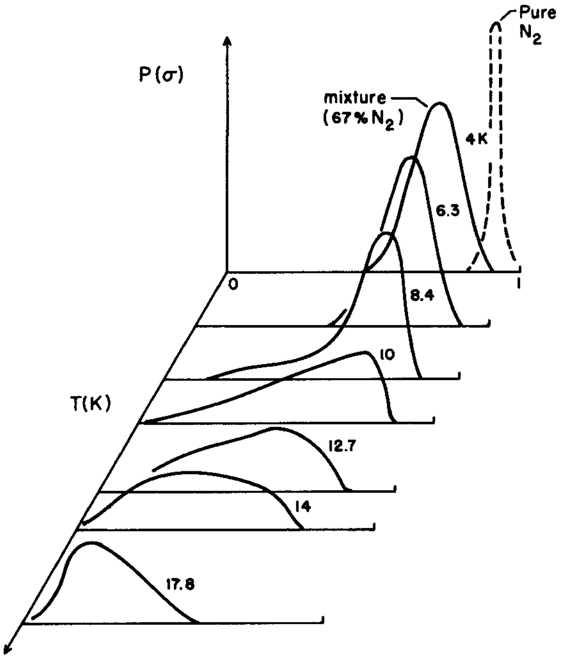

FIGURE 1 Temperature variation of the order parameter distribution function $P(\sigma)$ deduced from the analysis of the NMR line shapes reported in Reference 12 for a N_2-Argon solid mixture ($X_{N2} = 0.67$).

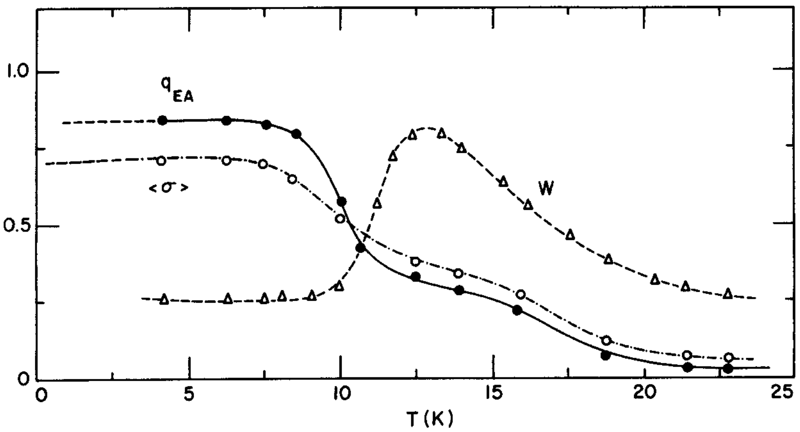

FIGURE 2 Temperature dependence of the Edwards-Anderson order parameter $q_{EA}(T)$ and the mean value $\langle\sigma\rangle T$ calculated from the order parameter distribution functions $P(\sigma)$.

Section I above, we identify $M_2(T)$ with the Edwards-Anderson order parameter $q_{EA}(T)$. We have also shown the variation of width W of the distribution function with temperature.

Although the temperature dependence of the parameters is smooth and there is no abrupt phase transition, two important features emerge from this analysis of the data. The first feature is that the temperature dependence is much stronger than that reported for a non-collective random quadrupolar field model.[21,23] This is illustrated in Figure 3 where we compare $q_{EA}(T)$ and $\langle\sigma(T)\rangle$ with the calculated dependences $q^{calc}(T)$ and $\langle\sigma\rangle^{calc}$ for the random field model.[23] The variations in the experimentally observed parameters over the interval $8 < T < 12$ K is much stronger than the variation of the calculated parameters.

The second feature of importance is the "saturation" of the order parameter distribution at 8 K, i.e., $P(\sigma)$ ceases to evolve below 8 K but *remains* much broader than the $P(\sigma)$ observed for the long range ordered Pa_3 phase. This means that a large fraction of the quadrupoles are not fully (i.e. 100%) aligned along their principal axes, and they continue to fluctuate about the mean position on cooling well below the transition region. The residual width of the distribution also shows that the degree of alignment varies from one site to another and that it persists to very low temperatures.

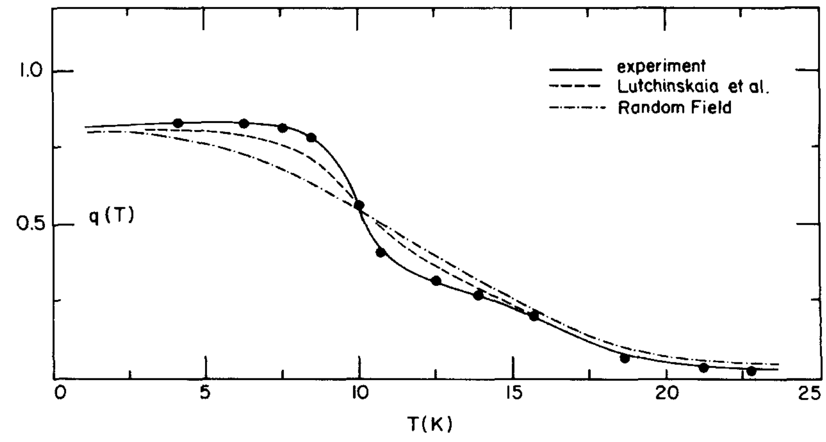

FIGURE 3 Comparison of the Edwards-Anderson glass order parameter $q_{EA}(T)$ obtained from the experimental data with the calculated values for a random mean field model and for the simplified glass model of Kokshenev[22] and Lutchinskaia et al.[23] (The calculated curves have been normalized to match the experimental data at low temperature.)

The most detailed calculations of the expected variation of the glass order parameter for quadrupoles is that published by Kokshenev.[21] (The model used by Kokshenev is similar to the Sherrington-Kirkpatrick model[25] for spin glasses and an earlier version can be found in Reference 24.) As shown in Figure 4, Kokshenev's results provide a very good qualitative description of the experimental data despite the assumptions made in the theory.

The results shown in Figures 3 and 4 are consistent with a model of a dynamical freezing[2] of the molecular rotational degrees of freedom rather than a thermodynamic phase transition. In this model the molecules become trapped in a limited but *non-unique* region of configuration space. Different regions of configuration space are accessed for different cooldowns. Transitions to neighboring (lower energy) configurations are inhibited by high energy barriers or the need to reorient many molecules simultaneously, i.e., via long narrow paths in configuration space. (The problem is like traveling in the European Alpine region before the construction of tunnels: you either took high mountain passes or chose tortuous routes linking long alpine valleys.) The evolutions seen in the Monte Carlo simulations carried out by M. Klenin and colleagues[9,10] also shows a strong collective nature and actually indicates a stronger transitional behavior than that so far detected experimentally.

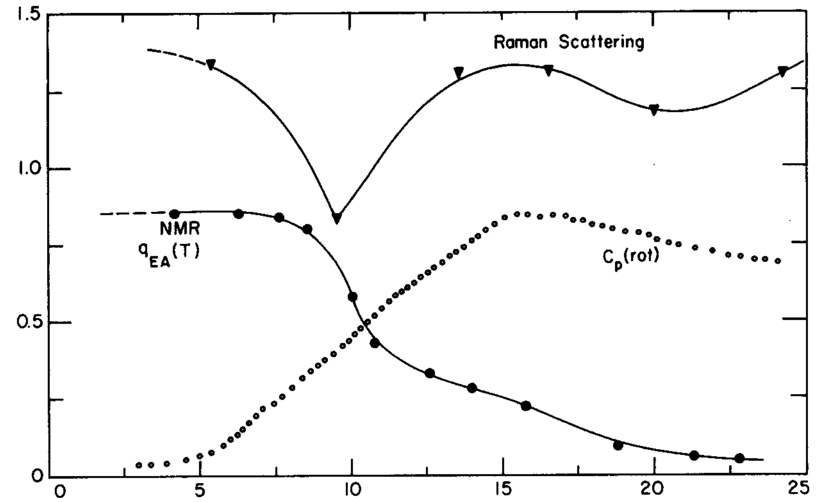

FIGURE 4 Comparison of the temperature dependence of the Raman scattering intensities observed by Long et al. (Reference 16), the heat capacity data (D. Haase et al., Reference 11) and the NMR data (D. Esteve et al., Reference 12).

The available experimental results are inadequate in that they do not test for two characteristic features expected for a glass phase:

(a) irreversibility, and

(b) residual ultra-slow motion at very low temperatures. Methods have been proposed to detect both features using stimulated echo techniques in NMR.[6] The echos become damped if slow molecular reorientations occur and although some effects have been reported, they are not convincing[6] and have not been successfully repeated.

Irreversibility has not been seen in the thermodynamic measurements carried out by Haase and co-workers[7,8] and it may be important to test for irreversibility over time scales significantly different to those used by Haase et al. for the heat capacity measurements. This can be done using AC caliorimetry or by studying the damping of NMR stimulated echos over different field cooling cycles.

If the system is trapped in a given global configuration and can tunnel to a neighboring state with a small but non-zero probability, then the heat capacity *and* the local order parameters will have a small low frequency time dependence. The observed specific heat would in that case be frequency dependent. The stimulated echoes are more sensitive to low frequency variations since the nuclear spin degrees of freedom are prepared by a special pulse sequence to record a "fingerprint" of the local orientational order. The focusing of the magnetisation after a time delay will occur only if the "fingerprint" remains undistorted and very small perturbations can in principle be detected.

Field cooling techniques which have played an important role in spin glasses can also be explored by the use of NMR methods. After cooling the system into one global configuration, a "fingerprint" of the orientations is taken with the preparatory pulses of the stimulated echo. The system can then be cycled over a small temperature interval, with or without an applied quadrupolar stress. If there is indeed a hierarchy of configurations the molecules find a new configuration and the stimulated echo will be dampened. The damping of the stimulated echo over various field cooling cycles can therefore be used to test for intrinsic glass behavior and non-ergodic behavior in the system. These experiments would be able to distinguish an orientational glass from a completely disordered para-orientational phase since the latter would always show reversibility over a small field cooling cycle.

In addition to the NMR experiments and heat capacity measurements, solid N_2-argon mixtures have also been studied using neutron scattering[11] and Raman scattering.[16] All of the experimental results show a smooth quenching of the rotational degrees of freedom on cooling through the 8–15 K temperature interval. The Raman scattering shows particularly sharp temperature dependencies at small wave numbers (10–20 cm^{-1}) and is consistent with the NMR results (see Figure 4). Only a small effect is seen in the 45–60 cm^{-1} range and no significant feature is seen at 80 cm^{-1}. This is not completely understood at present.

References

1. A. B. Harris and H. Meyer, *Com. J. Phys.*, **63**, 3 (1985).
2. N. S. Sullivan, *A.I.P. Conf. Proc.*, **103**, 109 (1983).
3. J. R. Gaines and P. E. Sokol, *A.I.P. Conf. Proc.*, **103**, 84 (1983).
4. S. Washburn, M. Calkins, H. Meyer and A. B. Harris, *J. Low Temp. Phys.*, **53**, 585 (1983); A. B. Harris, S. Washburn and H. Meyer, *J. Low Temp. Phys.*, **50**, 151 (1983).
5. D. Esteve, M. Devoret and N. S. Sullivan, *J. Phys. C.* (*Solid State*) **15**, 5455 (1982). See also M. Devoret, Ph.D. Thesis, Univ. of Paris unpublished.
6. N. S. Sullivan, D. Esteve and M. Devoret, *J. Phys. C.* (*Solid State*) **15**, 4895 (1982).
7. D. G. Haase, L. R. Perrell and A. M. Saleh, *J. Low Temp. Phys.*, **55**, 283 (1984).
8. L. G. Ward, A. M. Saleh and D. G. Haase, *Phys. Rev.*, B**27**, 1832 (1983).
9. M. Klenin, *Proc. XVII Intl. Conf. Low Temp. Physics*, **E14**, 1009 (1984).
10. M. Klenin, *Phys. Rev.*, **B28**, 5199 (1983).
11. W. Press, B. Janik and H. Grimm, *Z. Phys.*, **B49**, 9 (1982).
12. D. Esteve, N. S. Sullivan and M. Devoret, *J. de Phys.*, (Paris) **43**, L-793 (1982).
13. J. R. Brookeman and N. S. Sullivan, *Bull. Am. Phys. Soc.*, **30**, 613 (1985).
14. J. L. Yarnell, R. L. Mills and A. F. Schuch, *Sov. J. Low Temp. Phys.*, **1**, 366 (1974).
15. J. V. Gates, P. R. Granfors, B. A. Fraas and R. O. Simmons, *Phys. Rev.*, **B19**, 3667 (1979).
16. T. Long, Ph.D. Thesis, Univ. of Delaware; and T. Long and W. B. Daniels, to be published.
17. N. S. Sullivan, M. Devoret, B. P. Cowan and C. Urbina, *Phys. Rev.*, **B17**, 5016 (1978).
18. N. S. Sullivan and J. M. Vaissiere, *Phys. Rev. Lett.*, **51**, 658 (1983); See also Y. Lin and N. Sullivan, submitted to *J. Low Temp. Phys.*
19. G. E. Pake, *J. Chem. Phys.*, **16**, 327 (1948).
20. S. F. Edwards and P. W. Anderson, *J. Phys. F.* (*Metals*) **5**, 965 (1975).
21. V. B. Kokshenev, *Solid State Commun.*, **44**, 1593 (1982).
22. V. B. Kokshenev, *Sov. J. Low Temp. Phys.*, **11**, 881 (1985).
23. E. A. Lutchinskaia, V. N. Ryzhov and E. E. Tareyeva, *J. Phys. C* (*Solid State*) **17**, L-665 (1984).
24. N. S. Sullivan and M. Devoret, *Proc. Intl. Quant. Crystals Conf.*, E4, Col. State Univ., Fort Collins, Aug. 1977.
25. D. Sherrington and S. Kirkpatrick, *Phys. Rev. Lett.*, **35**, 1972 (1975).