

Explanation for the universal low-temperature and dynamical properties of a particular glass

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We present new measurements of the time-dependent specific heat of cubic $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$. Using a microscopic model of the tunneling centers (180°CN^- reorientations), we provide a unified explanation of this specific heat and the low-frequency dielectric loss. Thus, in a crystal exhibiting the universal low-temperature thermal properties and the broad low-frequency dielectric relaxations characteristic of glasses, we have explained both using a microscopic tunneling model.

Low-temperature properties of glasses appear to be dominated by tunneling centers. The tunneling-center models¹ have explained the logarithmic time dependence and linear temperature dependence of the specific heat and the T^2 dependence of the thermal conductivity. Two topics, untouched by these early theories, have remained mysteries: the microscopic *structure* of the tunneling centers and the universal *density* of the active centers (as deduced from low-temperature thermal measurements in glasses). Low-frequency dynamical properties of glasses and other amorphous systems have been modeled using several different approaches.² These theories relate the low-frequency properties to the liquid-glass transition. Each has its own explanation for the broad distribution of relaxation times found in these systems; these explanations are very general and material independent.

While universal properties should not depend on details of the particular glass, the converse is also true—an explanation for a universal property must apply to each individual glass: for example, to $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$. Cubic $(\text{KBr})_{1-x}(\text{KCN})_x$, for $0.1 < x < 0.6$, freezes into a disordered state at low temperatures, and this state has glassy low-temperature thermal properties.^{3,4} In this paper, we relate the low-frequency dielectric properties^{5,6} of $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$ observed above 10 K to the universal low-temperature properties. (We are not concerned with the controversial glass transition.) We determine the microscopic structure of the tunneling centers and the density of active centers in this glassy crystal. We report new experimental results, including extensive measurements of the time-dependent specific heat. Much of the theoretical basis of this paper has appeared as speculations in previous work,^{3,4,6-10} we have turned these speculations into a quantitative calculation. Thus, at least for this particular glassy material, we provide a microscopic explanation for the observed broad distribution of relaxation times and we resolve both outstanding mysteries in the tunneling theories of glasses.

In the pure alkali cyanides, cyanide-cyanide interactions cause a phase transition in which the cyanide axes (quadrupoles) align, remaining free to reorient by 180° .¹¹ The corresponding dielectric-loss peak is well described by mean-field theory;⁷ the reorientations are thermally activated, with the barrier height V a direct measure of the (quadrupolar) orientational order among the neighboring cyanide ions. This loss peak in $(\text{KBr})_{1-x}(\text{KCN})_x$ continuously broadens

(to 8–10 decades full width at half maximum) and shifts⁵ as the cyanide concentration x is lowered. At $x = 0.5$, the peak can be well described in terms of thermally activated crossing over barriers V with a Gaussian distribution $P(V)$:

$$P(V) = (\sqrt{\pi}\sigma)^{-1} \exp\left[-\frac{(V - V_0)^2}{\sigma^2}\right], \quad (1)$$

where V_0 is 659 K and σ is $300 \text{ K} - 1.5T$.⁶

Since the loss peak broadens smoothly and continuously as x decreases, it is natural to assume that the peak is still due to 180° reorientations; the axes are frozen by the strong elastic couplings. Thus the low-frequency dielectric behavior is insensitive to the disappearance of long-range order. Furthermore, we have found that the glassy low-temperature thermal properties also occur at $x = 0.7$, where the cyanide orientations have long-range order: The thermal conductivity shows the same T^2 form below 1 K and the same plateau between 2 and 10 K as does the $x = 0.25$ sample; the specific heat shows a (small) time-dependent term linear in T . Thus the glassy low-temperature thermal behavior and the glassy low-frequency dielectric behavior are both insensitive to the presence of long-range crystalline orientational order. Our theory is an extension of the mean-field theory for pure KCN to include some of the effects of disorder: We interpret the mean-field strength as a measure of the *local* orientational order. It does not distinguish between the glassy and ordered states, and is not a model for the glass transition.

The orientational order in the cyanides is described by a quadrupolar mean field. (The details of the theory will be published separately.)¹² The coupling of an ion to this mean field will be a sum of contributions from the (randomly distributed) first- and second-nearest-neighbor cyanides. If these contributions are roughly uncorrelated, we can use the central limit theorem to justify a Gaussian distribution of coupling constants. Each cyanide will have two stable orientations in the strain field. The barrier height V to 180° cyanide reorientations is proportional to the coupling constant, which naturally explains the log-normal form for the dielectric-loss peak [Eq. (1)]. To check if the fluctuations are large enough to explain the width of the peak, we can make the rough approximation of equal contributions from the 12 nearest neighbors: the ratio of the width to the peak of the resulting (nearly Gaussian) binomial distribution is $1/\sqrt{6}$. This prediction is 12% smaller than the

($T=0$) experimental ratio σ/V_0 . The temperature dependence of σ is due to the increasing thermal disorder in the neighboring cyanides, and is predicted within a factor of 2 by the theory. Thus our theory explains the form, width, and temperature dependence of the dielectric-loss peak.

Figure 1 shows the time dependence of the measured specific heat at $x=0.5$ over five decades of time t ; similar data have been obtained for $x=0.25$ and 0.7 . The solid curves in Fig. 1 are best fits of the form $C=C_1T+C_D T^3$; $C_D=196 \text{ erg/gK}^4$ is the phonon contribution calculated from elastic measurements.¹³

We will explain the time-dependent specific heat in terms of the same 180° cyanide reorientations that cause the dielectric-loss peak. We can use the distribution of barrier heights in Eq. (1) to estimate the number of active tunneling centers on a given time scale. A straightforward WKB estimate¹⁴ shows that the tunneling rate for barrier heights $V > V_{1 \text{ sec}}=96 \text{ K}$ will be slower than 1 Hz. Thus, for $x=0.5$, only the 0.35% of the ions with barriers less than 96 K in Eq. (1) will be able to tunnel in an experiment done on a 1-sec time scale.¹⁵ Of all the CN^- ions which are mobile on a certain time scale t_0 (i.e., which have barriers lower than V_{t_0}), only those with energy splittings $\leq k_B T$

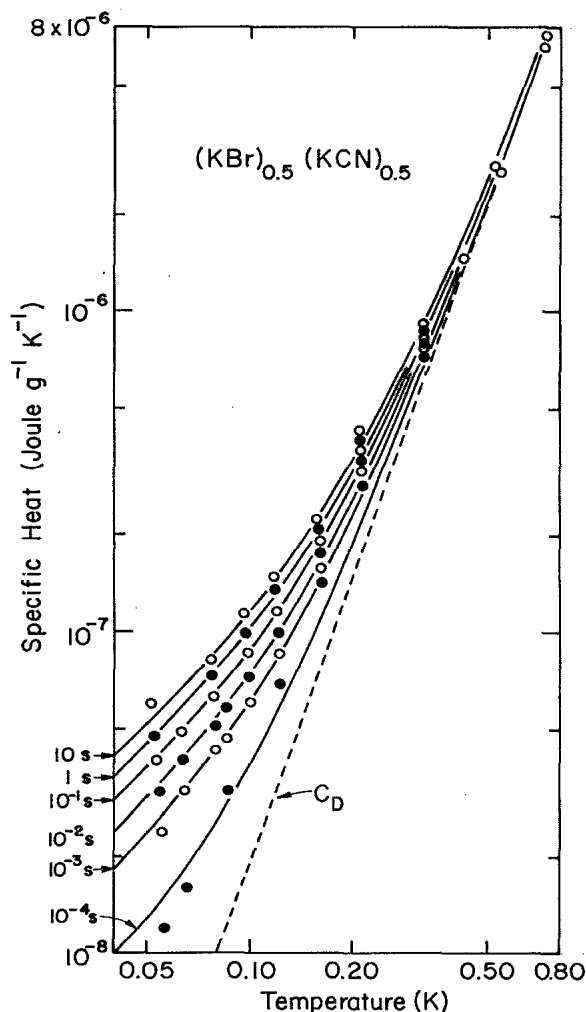


FIG. 1. Specific heat, determined from the temperature rise of the quasiadiabatic sample after the times t indicated. The curves are of the form $C=C_1T+C_D T^3$, where C_D is the Debye value determined from elastic measurements.

can contribute to the specific heat; the others are frozen out. The density of states in this range should be nearly constant and nonzero, leading to the term C_1T in the specific heat. We do not have a direct experimental probe of the distribution of asymmetries, but since they are due to dipole-dipole couplings, the inverse density of states should be given roughly by the asymmetry energy between the two orientations in the pure-cyanide antiferroelectric phase. This has been measured recently¹⁶ to be $\sim 340 \text{ K}$. Thus the CN^- ions with barriers $V < 96 \text{ K}$ will be spread over the asymmetry range $A_{\text{max}}=340 \text{ K}$, leading to a density of active tunneling centers per unit energy of $(0.0035 \text{ centers})/(340 \text{ K})$, assuming a uniform distribution over the asymmetry range. A fit to the 1-sec specific heat is achieved with only a slightly higher density, i.e., a smaller $A_{\text{max}}=292 \text{ K}$. The time-dependent $C_1(t)$ calculated without further adjustments agrees well with the data shown in Fig. 2. The standard models¹ assume a constant density of states \bar{P} per unit of volume, of tunneling exponent, and of asymmetry energy. They predict a straight line,¹⁷

$$C_1(t) = \frac{\pi^2}{12} k_B^2 \bar{P} \ln(4t/\tau_{\text{min}}), \quad (2)$$

which also fits the data well (although it has the additional free parameter τ_{min}).¹⁸

Finally, we reconcile¹⁹ the magnitude of the thermal conductivity^{3,4} [$\Lambda(T) \approx T^2$] with that predicted by the tunneling models, and we discuss the low-temperature dielectric constant [$\Delta\epsilon'/\epsilon' \approx \ln(T)$].²⁰ Since the thermal conductivity is dominated by centers with especially low barriers, it is sensitive to crystal-field effects which are negligible for the specific heat. Although this makes a detailed calculation of Λ difficult, we shall estimate it roughly using the standard model, which predicts¹⁸

$$\Lambda = \frac{\rho k_B^3 T^2}{6\pi\hbar^2 \bar{P}} \sum_i \frac{v_i}{\gamma_i^2}. \quad (3)$$

Here ρ is the mass density and v_i is the speed of sound of the i th phonon polarization, coupled to the tunneling states with coupling constant γ_i . We write the sum in (3) as $3v_D/\bar{\gamma}^2$, where v_D is the Debye speed of sound. We mea-

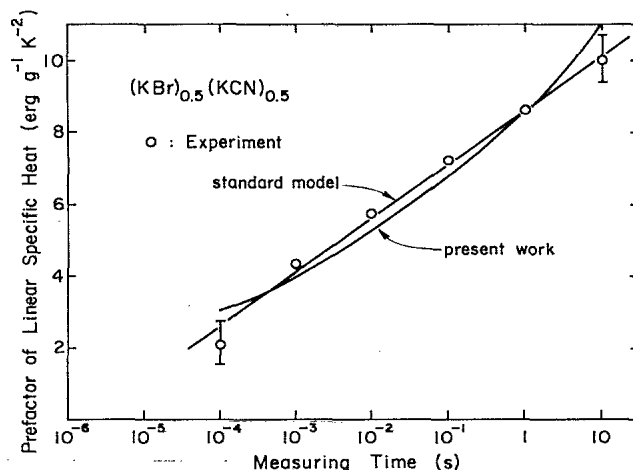


FIG. 2. Open circles: $C_1(t)$, the prefactors of the linear specific-heat anomaly shown in Fig. 1, compared with the predictions of the standard tunneling model and of the present work. The standard model has both slope and intercept as free parameters, while the microscopic model has only the overall vertical scale to adjust; the magnitude of this adjustment can be estimated within a factor of 2.

sure the coefficient of T^2 in $\Lambda(T)$ to be 9.5, 17, and $7.5 \times 10^{-4} \text{ W cm}^{-1} \text{ K}^{-3}$ for $x=0.25, 0.5,$ and 0.7 . Given this and $\bar{P}=4, 0.8,$ and $0.2 \times 10^{-32} \text{ erg}^{-1} \text{ cm}^{-3}$ from the time-dependent specific heat (roughly the slope of the straight line in Fig. 2), the effective coupling $\bar{\gamma}$ can be computed: $\bar{\gamma}=0.12, 0.18,$ and 0.54 eV , respectively. The first two values are comparable to the components of the strain coupling tensor for an isolated cyanide, which are about 0.15 eV .²¹ Thus the magnitude of the glassy thermal conductivity can be extrapolated from the dilute limit, at least until long-range order sets in. The dielectric constant ϵ' has been measured⁴ for $x=0.1$ and 0.2 , and a glassy logarithmic temperature dependence was observed. If we extrapolate our determination of $\bar{P}(x)$ to these concentrations, the electric dipole moment necessary to fit the data is $\mu=0.3 \text{ D}$; the accepted value for low concentration CN^- in KBr is 0.5 D —a reasonable agreement.

To conclude, we have convincingly linked the low-frequency dielectric-loss behavior and the time-dependent low-temperature specific heat in $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$. Both are simply due to 180° reorientations of individual CN^- ions (activated thermally and mediated by quantum tunneling, respectively). These reorientations are hindered by a

Gaussian distribution of barrier heights stemming from the cyanide-cyanide elastic interactions.

What have we learned about structural glasses? First, ordinary point tunneling centers can cause glassy behavior. Many exotic centers have been proposed; these are not ruled out, but are not universally necessary. Second, starting from roughly one center per atom, the magnitude of the specific heat of this system naturally assumes a value characteristic of glasses. Not only do we have a microscopic explanation of the density of active centers, but we also have a natural connection between the tunneling centers and the zero-temperature entropy of glasses.²² Third, the low-frequency dynamics of glasses may be connected to thermally activated reorientations of similar centers. By studying a particular glass, we may have gained insight into glasses in general.

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¹¹J. M. Rowe, J. J. Rush, and S. Susman, *Phys. Rev. B* **28**, 3506 (1983). In addition to the orthorhombic ferroelastic phase seen for $x > 0.95$, they see regions of an "antiferroelastic" monoclinic phase at lower concentrations. These partial phase transitions could explain the jump in the conductivity seen (Ref. 3) in the $x=0.25$ sample at 70 K. The theory presented here uses the local ordering only to estimate the scale of the couplings; there is no particular reason to believe the local order in the glass is any more monoclinic than it is orthorhombic, so we use the couplings from the pure cyanide.

¹²J. P. Sethna and K. S. Chow (unpublished).

¹³The "anomalous T^3 " term in the specific heat is experimentally

compatible with zero for $x=0.5$; it is nonzero at lower cyanide concentrations. The method of harmonic series expansion has been used: G. A. Alers, in *Physical Acoustics*, edited by P. W. Mason (Academic, New York, 1965), Vol. IIIB, p. 1. The low-temperature elastic constants have been extracted from R. Feile, A. Loidl, and K. Knorr, *Phys. Rev. B* **26**, 6825 (1982), and references therein; and from S. K. Satija and C. H. Wang, *Solid State Commun.* **28**, 617 (1978).

¹⁴We use the moment of inertia $2.65 \times 10^{-39} \text{ g cm}^2$ measured for the dilute cyanide impurities in KBr. This differs from the molecular moment by an effective-mass contribution from the dynamic deformation of the surrounding lattice. The phonon effects on this tunneling rate are excellently approximated by an effective mass [J. P. Sethna, *Phys. Rev. B* **24**, 698 (1981); **25**, 5050 (1982)].

¹⁵We are extrapolating the Gaussian far into the low barrier tail of the distribution ($V_0 - V \geq 2\sigma$). Experimentally, the distribution is valid 1.5σ out on the low barrier tail, and over 2.5σ out on the high barrier tail of the distribution [S. R. Nagel (private communication)]. We interpret the distribution (1) as the contribution to the barrier height from the cyanide-cyanide interactions (e.g., not including crystal-field contributions.)

¹⁶Lei Wu, Y. H. Jeong, and S. R. Nagel (private communication).

¹⁷We ignore the temperature dependence of τ_{min} ; it has small effects.

¹⁸J. L. Black, *Phys. Rev. B* **17**, 2740 (1978).

¹⁹Reference 3 noted a discrepancy between the thermal conductivity and the short-time specific heat at $x=0.25$; we show here that this discrepancy disappears under closer analysis (although one still exists at $x=0.7$).

²⁰For details, see J. J. DeYoreo, Ph.D. thesis, Cornell University, 1985 (unpublished).

²¹This is the strain coupling of an isolated CN^- ion in KBr to a shear wave in the $\langle 100 \rangle$ direction. It is given by $\frac{1}{3}(\lambda_1 - \lambda_2)V_0c_{44}$, where V_0 is the volume of the primitive unit cell (70 \AA^3 in KBr) and c_{44} is the shear modulus. The elastic dipole shape factor $\lambda_1 - \lambda_2$ is from H. U. Beyeler, *Phys. Rev. B* **11**, 3078 (1975).

²²The residual entropy in many glasses has been measured by integrating the specific heat; it is $k_B \times$ (the number of molecular units), up to a constant of order one. This suggests that each unit has a few equilibrium positions, i.e., there is roughly one tunneling center per unit.