Tunneling States in Crystals with Large Random Strains

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The two-level systems (TLS) that dominate the low temperature properties of amorphous solids have two features, both of which are unexplained—(i) a constant density of states with (ii) nearly the same magnitude in all amorphous solids. We show that feature (i) can also arise in lightly doped crystals subjected to internal strains: A KCl or KBr crystal doped with ~1 mole% KCN has a narrow spectrum of tunneling states. When random internal strains are introduced by substituting Br^- ions for half of the Cl^-, however, these tunneling states are replaced by TLS showing feature (i) of amorphous solids.

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The low temperature ($T \leq 1$ K) lattice vibrations of amorphous solids are dominated by tunneling states, also known as two-level systems (TLS). Their physical origin is still in question, as is the importance of interactions between the TLS [1–3]. Investigations of crystals with controlled amounts of disorder, e.g., $(KBr)_{1-x}(KCN)_x$ mixed crystals, also have not led to unambiguous answers regarding the mechanisms leading to the TLS. A substantial body of theoretical work [4], molecular dynamics simulations [5], and experiment [6] have significantly clarified the importance of both interactions and random strain on the high temperature ($\gtrsim 90$ K) orientational phase transitions in these materials. By contrast, the role of static random strain on the low temperature properties has only recently been addressed [7]. In this Letter we demonstrate experimentally that in crystalline solids, static random strains can change the states of relatively isolated tunneling defects into a broad spectral distribution of tunneling states very similar to that found in all amorphous solids. This observation underscores the importance of the local variations of the interatomic potential, rather than interactions between defects, as a possible cause of the broad distributions.

CN^- ions substituted for Cl^- or Br^- in KCl and KBr, respectively, can tunnel between different equivalent orientations which are separated by potential barriers of energy 35 K × k_B (24 cm^{-1}) [8]. The tunneling states, spaced by ~1 to 2 cm^{-1}, are seen as Schottky anomalies in specific heat and by resonance phonon scattering in thermal conductivity experiments [8]. For $\leq 0.1\%\, CN^-$, the ions can be considered as isolated, noninteracting defects with identical energy spectra [9]. Even up to 1%, the highest concentration to be used here, the perturbations of the tunneling states will be shown to be negligible for the present purpose [10]. Because of the disparity in ionic radii of Cl^- and Br^-, mixed crystals of KCl and KBr are heavily strained, yet fully miscible. In order to maximize the static random internal strain (estimated below), KCl was mixed with KBr in approximately equal parts. Sample preparation and experimental techniques are discussed elsewhere [12]. The unique contribution of the present work is that random strains and interactions between TLS can be varied independently in this system—the former by varying the relative concentrations of KCl and KBr, and the latter by varying the CN^- concentration. For this study, the CN^- concentration was kept low enough so that random strain dominates.

The effects of random strain on the thermal conductivity, specific heat, and internal friction of crystals with and without CN^- doping are shown in Figs. 1–3. In the unstrained crystal $(KBr)_{0.997}(KCN)_{0.003}$, there is strong resonant scattering in the thermal conductivity near 500 mK due to the CN^- ion tunneling states (Fig. 1, curve *e*). The random internal strain of the $(KCl)_{0.5}(KBr)_{0.5}$ host crystal has a dramatic effect on these states: The strong resonant scattering has almost completely vanished and is replaced by a T^2 temperature dependence below 1 K (open symbols), very similar to amorphous solids and to substitutionally disordered crystals with glasslike lattice vibrations. Data for $(KBr)_{0.59}(KCN)_{0.41}$ are shown as an example of the latter (curve *d*) Even above 1 K, the thermal conductivity of $(KCl)_{0.5}(KBr)_{0.5}$ + 0.9% CN resembles that of amorphous solids in that it shows no peak, but a hint of the plateau seen in many amorphous solids. Also shown in Fig. 1 are data for undoped $(KCl)_{1-x}(KBr)_x$ (solid circles and curves *a–c*), demonstrating that the substitution of Br^- for Cl^- has only a minor effect in the undoped mixed crystals, reducing the thermal conductivity at intermediate temperatures.

Specific heat data (Fig. 2) also reveal a dramatic difference in the energy spectra of the CN^- ions in the unstrained and heavily strained crystals. A Schottky anomaly appears in KCl doped with 0.06% KCN (curve *b*, dash-dotted line). The specific heat anomaly of KBr containing 0.8% KCN (curve *a*, dash-dotted line) is somewhat broader than that observed at the lower concentration in KCl, indicative of the spreading of the tunneling states caused by the higher doping. In $(KCl)_{0.5}(KBr)_{0.5}$ + 0.9% CN, however, the anomaly has almost completely vanished and has been replaced by a specific heat varying linearly with temperature, similar to that observed in amorphous solids. The

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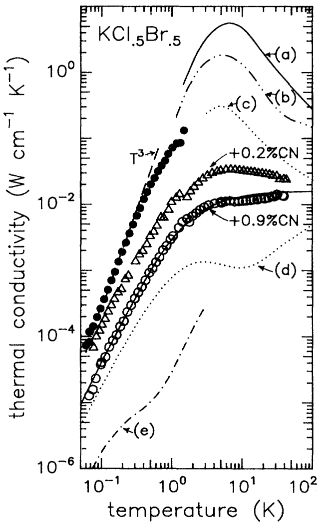

FIG. 1. The thermal conductivity of KBr doped with a small concentration of CN^-, $(KBr)_{.997}(KCN)_{.003}$ (curve *e*, Ref. [9]), shows strong resonant scattering near 500 mK due to a narrow spectrum of CN^- tunneling levels. A similar concentration of CN^- doped into the heavily strained crystal $(KCl)_{.5}(KBr)_{.5}$ gives T^2 glasslike behavior for both $(KCl)_{.5}(KBr)_{.5}$ +0.2% CN and $(KCl)_{.5}(KBr)_{.5}$ + 9% CN (this work); the data follow the tunneling model prediction, solid curve through circles (fit includes Rayleigh scattering, which is important above 1 K). In the heavily strained system, a broad spectrum of tunneling states exists, with correspondingly less scattering at any given temperature. Data for a mixed crystal with glasslike excitations, $KBr_{.59}CN_{.41}$ (curve *d*, Ref. [9]), are shown for comparison. The thermal conductivities of undoped $(KCl)_{1-x}(KBr)_x$ mixed crystals (curves (a)-(c)) have crystalline behavior, confirming that prior to the CN^- doping, no glasslike tunneling states are present (curve a): $x = 0$, curve (b): $x = 0.01$, Ref. [13]; curve (c): $x = 0.48$, Ref. [13] below 20 K, Ref. [15] above 20 K; solid circles $x = 0.55$, this work. The dashed line marked 'T^3 indicates the Casimir limit for the $x = 0.55$ sample. The slight dip near 40 K in curve (b) is due to resonant mode scattering from Br^- [13].

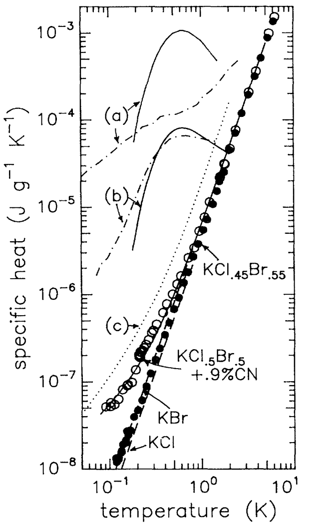

FIG. 2. The Schottky anomaly in KCl + 0.06% CN (curve *b*, dash-dotted line, Ref. [16]) is close to the expected contribution due to 0.06% CN^- (solid curve, based on ⟨111⟩-oriented CN^- ions with four energy levels of degeneracy 1-3-3-1 separated by 1.0 cm^{-1}), indicating a narrow energy spectrum for the CN^-. At higher doping in KBr + 0.8% CN (curve (a), dash-dotted line, Ref. [17]), the Schottky anomaly is somewhat broadened, presumably die to residual strain in this crystal and, perhaps, the onset of CN^- interactions; the specific heat is not glasslike. At similar doping in the heavily strained crystal, $(KCl)_{.5}(KBr)_{.5}$ + 0.9% CN (this work), the specific heat is glasslike: the Schottky anomaly is replaced by a linear contribution, indicating vastly different energy spectra for the CN^- ions, with a correspondingly smaller contribution to the specific heat at any given temperature. The solid curve through the open circles is a fit to the data: $c_1T + (c_3 + c_D)T^3$ with $c_1 = 5 \times 10^{-7}\ Jg^{-1}K^{-2}$, $c_3 = 1.2 \times 10^{-6}\ Jg^{-1}K^{-4}$, and $c_D = 4.8 \times 10^{-6}\ Jg^{-1}K^{-4}$ from the $(KCl)_{.45}(KBr)_{.55}$ data). Also shown are data for a mixed crystal with glasslike excitations, $(KBr)_{.59}(KCN)_{.41}$ (curve (c), Ref. [9]), crystalline T^3 behavior for $(KCl)_{.45}(KBr)_{.55}$ (this work), and Debye predictions for KBr [9] and KCl [8].

specific heat of the disordered crystal $(KBr)_{0.59}(KCN)_{0.41}$ (curve *c*) is again shown for comparison.

In Fig. 3, the internal friction of the doped, heavily strained crystal is shown to be similar to that of amorphous solids and distinctly larger than that of the undoped mixed crystal. In addition, the internal friction of $(KCl)_{0.5}(KBr)_{0.5}$ + 0.9% CN is significantly less than for the doped, unstrained crystal $(KBr)_{0.997}(KCN)_{0.003}$, where each CN^- has nearly the same energy spectrum.

Since the measurements on $(KCl)_{0.5}(KBr)_{0.5}$ + 0.9%CN resemble those obtained on amorphous solids, we have fit the data to the tunneling model predictions [19,20], as shown by the solid curves through the data in Figs. 1–3. The relevant parameters derived from the fit to the internal friction data are listed in Table I. The spectral density of TLS, $\overline{P}$, is similar to the value for amorphous solids and for mixed crystals with glasslike excitations.

The effects of strain on tunneling states have been observed previously. In crystalline $(NaBr)_{1-x}(NaF)_x$ with $x \leq 0.03\%$ F^-, for example, static random strains produce a slight asymmetry in the double well potential of the F^- tunneling center, sufficient to lead to a linear contribution to the specific heat [22]. The strain-induced effects, however, are too small to produce the universal glasslike properties. Recent experimental results on Kr:$^{14}N_2$:Ar indicate that static internal strains may have a comparable effect in this system as in $(KCl)_{0.5}(KBr)_{0.5}$ + 0.9% CN [23].

An estimate of the asymmetry energy of the CN^- ions gives a measure of the difference in their local environments in pure KBr or KCl versus the strained

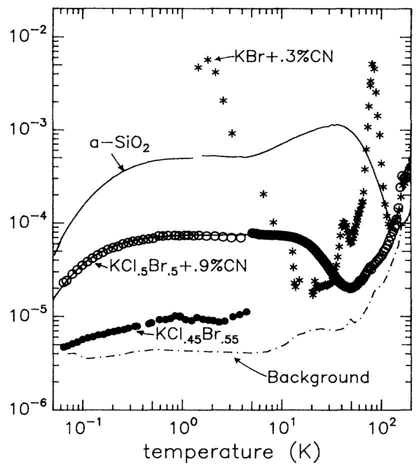

FIG. 3. Internal friction, Q^{-1}, of mixed crystals measured in torsion at 90 kHz. Data for pure $(KCl)_{.45}(KBr)_{.55}$ are close to the background loss due to the mounting arrangement, which has not been subtracted from the data sets. For KBr + 0.3% CN, where each CN^- ion has nearly the same energy spectrum, Q^{-1} is large and non-glasslike. Data for $(KCl)_{0.5}(KBr)_{0.5}$ + 0.9% CN, however, are similar to an amorphous solid, a-SiO_2 [18], and follow the Tunneling Model prediction (solid curve through data).

mixed crystal $(KCl)_{0.5}(KBr)_{0.5}$. The asymmetry energy $\triangle$, the difference in energy between the potential minima when a CN^- axis reorients, is given by

$$\gamma = \frac{1}{2}\frac{\triangle}{\epsilon}, \tag{1}$$

where γ is the coupling energy between TLS and strain and ϵ is the strain [20]. The asymmetry energy of the CN^- in the pure crystals KCl or KBr for low CN^- concentrations, where the CN^- orientations are equivalent, is zero. For the strain in the mixed crystal we use the difference in lattice constants between $(KCl)_{0.5}(KBr)_{0.5}$ (6.441 Å from x-ray measurements) and the lattice constant of either KBr (6.593 Å [12]) or KCl (6.293 Å [12]). Inserting the coupling constant from Table I, $\gamma = 0.11$ eV, we obtain an asymmetry energy $\triangle/k_B$ of 59 K (41 cm^{-1}) with respect to the lattice constant of KBr and 60 K (42 cm^{-1}) with respect to the lattice constant of KCl, a value comparable to the potential barrier for reorientation of a CN^- ion in KBr or KCl in the dilute limit, 35 K (24 cm^{-1}) [8]. It appears, therefore, that the internal strain field in $(KCl)_{0.5}(KBr)_{0.5}$ is large enough to significantly alter the crystal field, thereby redistributing the tunneling states of the CN^- ions.

As a rough determination of whether similar ideas may apply to amorphous solids as well as the heavily strained crystals, we can estimate the asymmetry induced by the internal strain in a-SiO_2, using the distribution of Si separations measured for that material [24]. The average strain is $\epsilon = \triangle a/a = 0.05$, where $\triangle a$ is the half-width of the distribution and a is the average Si separation. Using Eq. (1) and the value for γ_t listed in Table I, this leads to an asymmetry of $\triangle/k_B = 1200$ K, of the same order as a typical potential barrier of 600 K in a-SiO_2 [25].

An entropy calculation also reveals a significant difference between the energy spectra of the CN^- ions in pure KCl or KBr versus the strained mixed crystal $(KCl)_{0.5}(KBr)_{0.5}$. In KCl or KBr doped with 0.9% KCN, the energy spectra are similar, leading to a large, somewhat broadened Schottky anomaly (Fig. 2) and an entropy contribution per unit volume of

$$\frac{S}{k_B} = N \ln 8 = 1.4 \times 10^{20}\ \mathrm{cm}^{-3}, \tag{2}$$

where N is the CN^- concentration with eight equivalent $\langle 111 \rangle$ orientations for the CN^- ions. In the strained $(KCl)_{0.5}(KBr)_{0.5}$ host, the CN^- energy levels are spread over a broad range, leading to a small linear contribution to the specific heat c_1 (see Fig. 2 caption) and an entropy contribution of $\triangle S = c_1 \triangle T$, where $\triangle T$ is the temperature range over which the CN^- states are spread. Therefore, in order for the entropies to be identical,

$$\triangle T = \frac{N \ln 8}{c_1} = 3200\ \mathrm{K}. \tag{3}$$

This number, of course, is unphysically large and is only intended to convey the idea that of all the CN^- tunneling states that appear below 1 K in pure KBr or KCl doped with ~1% KCN, only a very small fraction, ~300 ppm, remain below 1 K in the strained mixed crystal, a value typical of mixed crystals with glasslike excitations.

TABLE I. Tunneling Model parameters γ_t (transverse coupling of TLS to phonons), $\overline{P}$ (spectral density of TLS), and the dimensionless ratio $\overline{P}\gamma_t^2/\rho v_t^2$ (ρ mass density, v_t transverse speed of sound) for $(KBr)_{0.59}(KCN)_{0.41}$ [9], a-SiO_2 [18], and $(KCl)_{0.5}(KBr)_{0.5}$ + 0.9% CN (this work, form internal friction data; values in parentheses are derived from a tunneling model to fit to the variation in the transverse speed of sound, $\delta v/v$). Values derived from $\delta v/v$ above its peak are typically ~50% larger than from internal friction data [21]).

Material	γ_t (eV)	$\overline{P}$ (10^{44} J^{-1} m^{-3})	$10^4\overline{P}\gamma_t^2/\rho v_t^2$
$(KCl)_{0.5}(KBr)_{0.5}$ + .9% CN	0.11	6(10)	0.45(0.74)
$(KBr)_{0.59}(KCN)_{0.41}$	0.18	9	1.5
a-SiO_2	0.65	8	2.8

It has been previously suggested that in systems like $(KBr)_{1-x}(KCN)_x$, static random strain is important both for the high temperature transition into the orientational glass state and for the low temperature tunneling states [4]. In regard to the connection between the high temperature phase transition and the appearance of TLS, it would be interesting to determine whether any remnant of a high temperature orientational glass transition even exists in $(KCl)_{0.5}(KBr)_{0.5}$ + 0.9% CN.

In summary, we have demonstrated experimentally that the broad energy distributions responsible for the low temperature glasslike properties can be manufactured for the mixed alkali-halide alkali cyanides by random strain fields in a crystalline lattice, even in the absence of significant interactions between the individual tunneling defects. The connection to amorphous solids, and, in particular, whether the assumption of random strains alone can explain the universal magnitude of the spectral density, will require further study.

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