

shows a behavior close to the undamped predictions, while the higher- I_c sample demonstrates the reduction of tunneling rates due to dissipation. This reduction is consistent with the temperature-dependent rates found in high-current-density junctions.⁹ The use of well characterized junctions [independent estimate of C and direct measurement of $R(T)$], the extension to very low temperatures, and the detailed measurement of $P(I)$ were important in being able to rule out extraneous effects and interpret the data within a theoretical framework. Although the observed reduction in tunneling rate ($A \approx 4.5$) is slightly greater than the expected $A \approx 1$, the magnitude is still reasonable. It is possible that the appropriate R in Eq. (5) is not the measured dc resistance near the origin (as used here) but either the high-frequency resistance or the quasiparticle resistance above the gap (in which case $A \approx 1.5$). Additional theoretical work is needed both on the effect of nonlinear and frequency-dependent damping and on the actual form of the crossover from thermal activation to macroscopic tunneling.

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Evidence for Elastic Disorder in the Elastically Ordered Phase of KCN

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We have obtained evidence from ^{13}C NMR measurements that the CN^- ion in the elastically ordered phase of KCN is misoriented slightly with respect to the orthorhombic b axis. This misorientation varies randomly over the lattice, averaging to zero on a macroscopic scale. The misorientations are manifested through small-angle CN^- reorientations which contribute to the spin-lattice relaxation time T_1 of the ^{13}C nuclei, via dipolar interactions and chemical shift anisotropy.

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Potassium cyanide (KCN) exhibits an elastically ordered phase (below 168 °K) in which the CN^- molecules are aligned parallel to the b axis in an orthorhombic crystal structure^{1,2} (see Fig. 1). In this phase, the CN^- molecules are disordered with respect to head-to-tail alignment and undergo random head-to-tail reorientations. The structure and dynamics of this system have been of considerable interest in recent years.³⁻⁷

We have studied this system by NMR of ^{13}C and from our results have been forced to conclude that, in the elastically ordered phase of KCN, *small*-angle reorientations as well as head-to-tail reorientations are taking place. This effect arises from the head-to-tail disorder of the CN^- molecules. Since the CN^- molecule is slightly different with respect to head and tail, this disorder breaks the orthorhombic symmetry of the

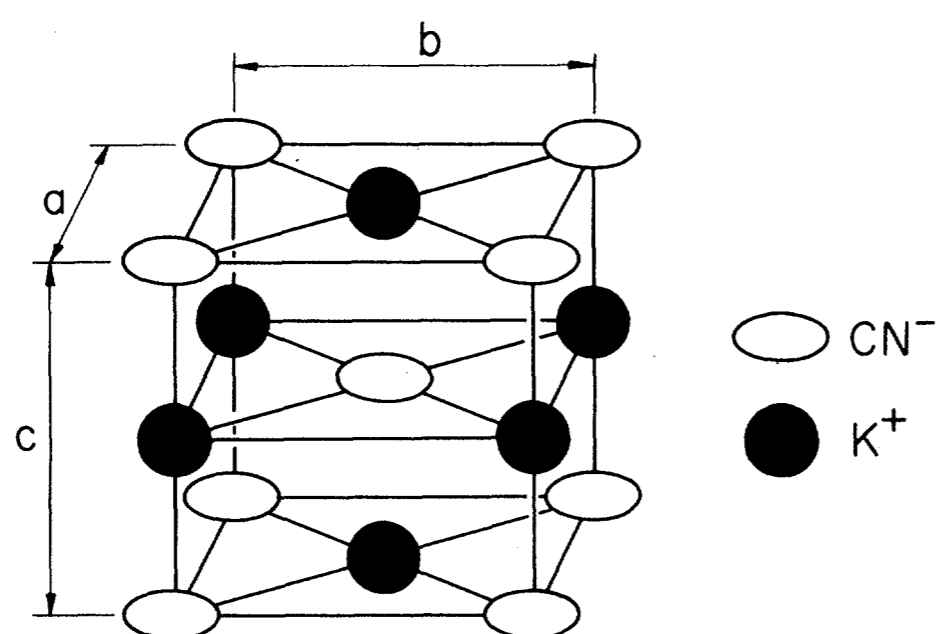


FIG. 1. Orthorhombic crystal structure of KCN: $a = 4.24 \text{ \AA}$, $b = 5.14 \text{ \AA}$, and $c = 6.16 \text{ \AA}$ (see Ref. 1).

lattice on a microscopic scale and causes a *local* distortion of the lattice. Each CN^- molecule is thus displaced slightly from its otherwise equilibrium orientation along the b axis. This displacement varies randomly from molecule to molecule such that, over *macroscopic* distances, the displacement averages to zero and the lattice has overall orthorhombic symmetry. Now, each time a CN^- ion reorients head to tail, the local distortion of the lattice changes, causing the CN^- mol-

ecules in the vicinity to adjust their orientations to a new angle with respect to the b axis. Also, for the same reason, the head-to-tail reorientations themselves may not be exactly 180° . Thus a given CN^- molecule reorients both in small steps (due to head-to-tail reorientations of neighbors) as well as large steps (due to its own head-to-tail reorientations). All these reorientations provide a source for ^{13}C nuclear spin-lattice relaxation in KCN.

The relaxation times T_1 were measured in isotopically enriched (90 at. % ^{13}C) powder samples of KCN obtained from Prochem (Summit, New Jersey). The results at three different fields are shown in Fig. 2. The field dependence of T_1 can be explained by considering two different interactions: the ^{14}N - ^{13}C dipolar interactions and the ^{13}C chemical shift,

$$\frac{1}{T_1} = \frac{1}{T_{1,\text{dip}}} + \frac{1}{T_{1,\text{CS}}} \quad (1)$$

Starting from general expressions⁸ for T_1 , we have derived the following result for CN^- reorientations in a powder sample:

$$\frac{1}{T_{1,\text{dip}}} = \frac{1}{5} \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) r^{-6} [J(\omega_I - \omega_S) + 3J(\omega_I) + 6J(\omega_I + \omega_S)] \quad (2)$$

and

$$\frac{1}{T_{1,\text{CS}}} = \frac{1}{5} \omega_I^2 (\Delta\sigma)^2 J(\omega_I) \quad (3)$$

Here, subscripts I and S refer to ^{13}C and ^{14}N , respectively. The terms ω_I and ω_S are the NMR frequencies, $\gamma_I H_0$ and $\gamma_S H_0$, of these nuclear spins in an external dc magnetic field H_0 . The term r is the C-N distance, and $\Delta\sigma$ is the anisotropy of the ^{13}C chemical shift tensor. $J(\omega)$ is the spectral density function of the CN^- reorientations:

$$J(\omega) = \int_0^\infty d\tau \cos(\omega\tau) \{ \langle [\hat{r}(t) \cdot \hat{r}(t+\tau)]^2 \rangle_t - C \}, \quad (4)$$

where \hat{r} is a unit vector along the direction of the C-N axis, and C is a constant chosen so that the integrand vanishes at $\tau = \infty$. The average is taken over time t .

Since $\omega_I \gg \omega_S$, we obtain from Eqs. (2) and (3)

$$\frac{T_{1,\text{dip}}}{T_{1,\text{CS}}} \cong \frac{\omega_I^2 (\Delta\sigma)^2 r^6}{10 \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1)}, \quad (5)$$

which is independent of $J(\omega)$ and thus of the nature of the reorientations. We see that at low field (small ω_I) the dipolar contribution dominates T_1

(i.e., $T_{1,\text{dip}}^{-1} > T_{1,\text{CS}}^{-1}$) whereas at high field the chemical shift dominates. Using $\Delta\sigma = 290$ ppm (Ref. 9) and $r = 1.05 \text{ \AA}$ (Ref. 1), we calculate that $T_{1,\text{dip}} = T_{1,\text{CS}}$ at $\omega_I/2\pi = 29$ MHz. At this frequency the T_1 minimum should have a value larger than the T_1 minima at frequencies above or below. This result is in agreement with our data for 24 MHz which is intermediate between the two extremes of either $T_{1,\text{dip}}$ or $T_{1,\text{CS}}$ dominating T_1 . This agreement establishes firmly the fact that the observed relaxation is due to CN^- reorientations and is thus given by the expressions in Eqs. (2) and (3).

The function $J(\omega)$ depends on the nature of the reorientations. Note that $J(\omega) = 0$ for a simple head-to-tail reorientation. This is due to the fact that *both* the intramolecular dipolar energy and the chemical shift tensor are invariant under 180° rotations. Thus, our observed relaxation must be due to some other reorientations.

We first consider the possibility that the CN^- molecule reorients head to tail via intermediate potentials wells (for example, in the $\langle 111 \rangle$ orthorhombic directions, as suggested by Von der

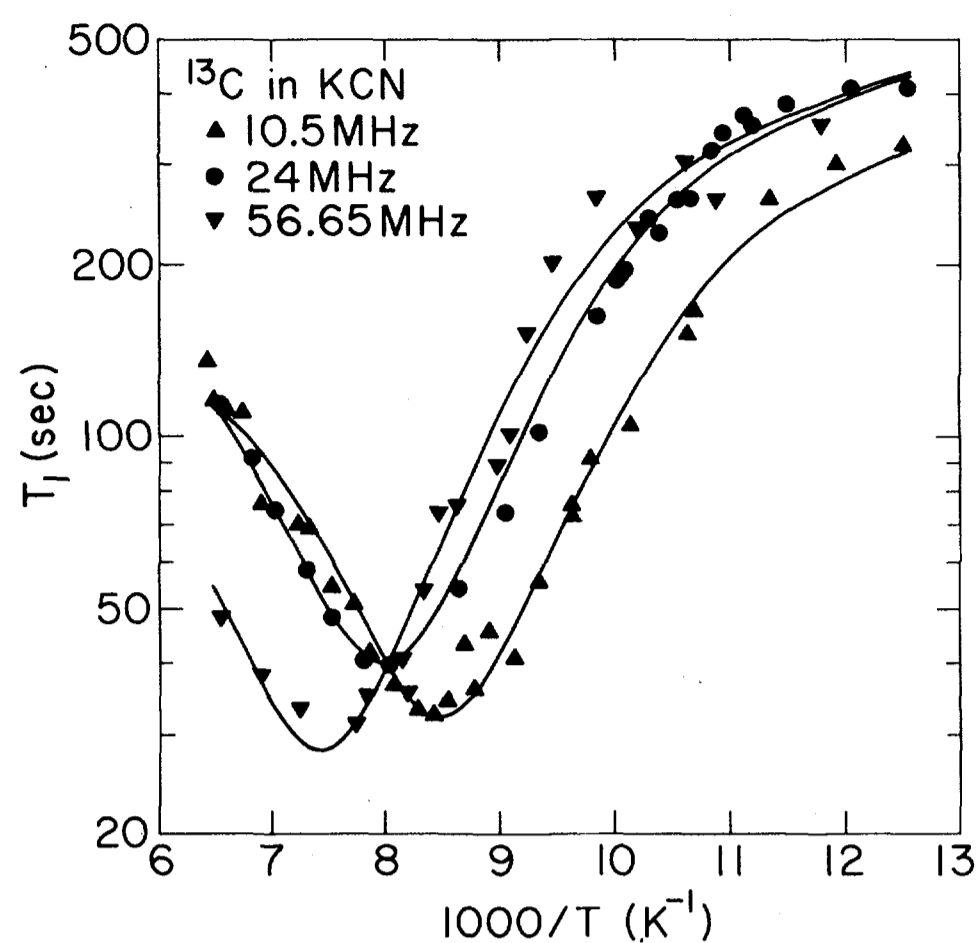


FIG. 2. ^{13}C spin-lattice relaxation time T_1 as a function of temperature at three different fields. Solid lines are the least-squares fit of Eq. (1) to the data.

Weid *et al.*³). Such reorientations between potential wells of unequal depth would produce some rather unusual features¹⁰ in T_1 , which we do not observe in our data. Hence, we can rule out this possibility. We will discuss this point in more detail in a later paper.

Thus, to explain our relaxation data, we are forced to consider reorientations of the type proposed at the beginning of this Letter, i.e., small-step and large-step reorientations which arise from the small elastic disorder of the lattice. Using this model, we obtain

$$J(\omega) = 2\alpha_{\text{rms}}^2 \frac{\tau_c}{1 + \omega^2 \tau_c^2}, \quad (6)$$

where τ_c is the correlation time of the CN^- reorientations and α is the angle between the C-N and b axes. Therefore, α_{rms} is a measure of the average misorientation of the CN^- molecules with respect to the b axis.

We obtain τ_c from the position of the T_1 minima, which occur at $\omega_I \tau_c \cong 1$. From our data, we thus obtain τ_c at three different temperatures. We also obtain values of τ_c from dielectric response measurements of Julian and Luty,^{4,11} assuming $\omega \tau_c \cong 1$ at the Debye loss peak. Plotting all these values of τ_c in Fig. 3, we see that τ_c obeys an Arrhenius relationship, $\tau_c = \tau_0 \exp(E_A/kT)$. From a least-squares fit, we obtain $E_A = 0.134$ eV and $\tau_0 = 2.6 \times 10^{-14}$ s.

We note here that at 80 °K KCN undergoes a second-order phase transition below which the CN^- molecules are aligned with respect to head and tail in an antiparallel fashion.^{5,12} In this

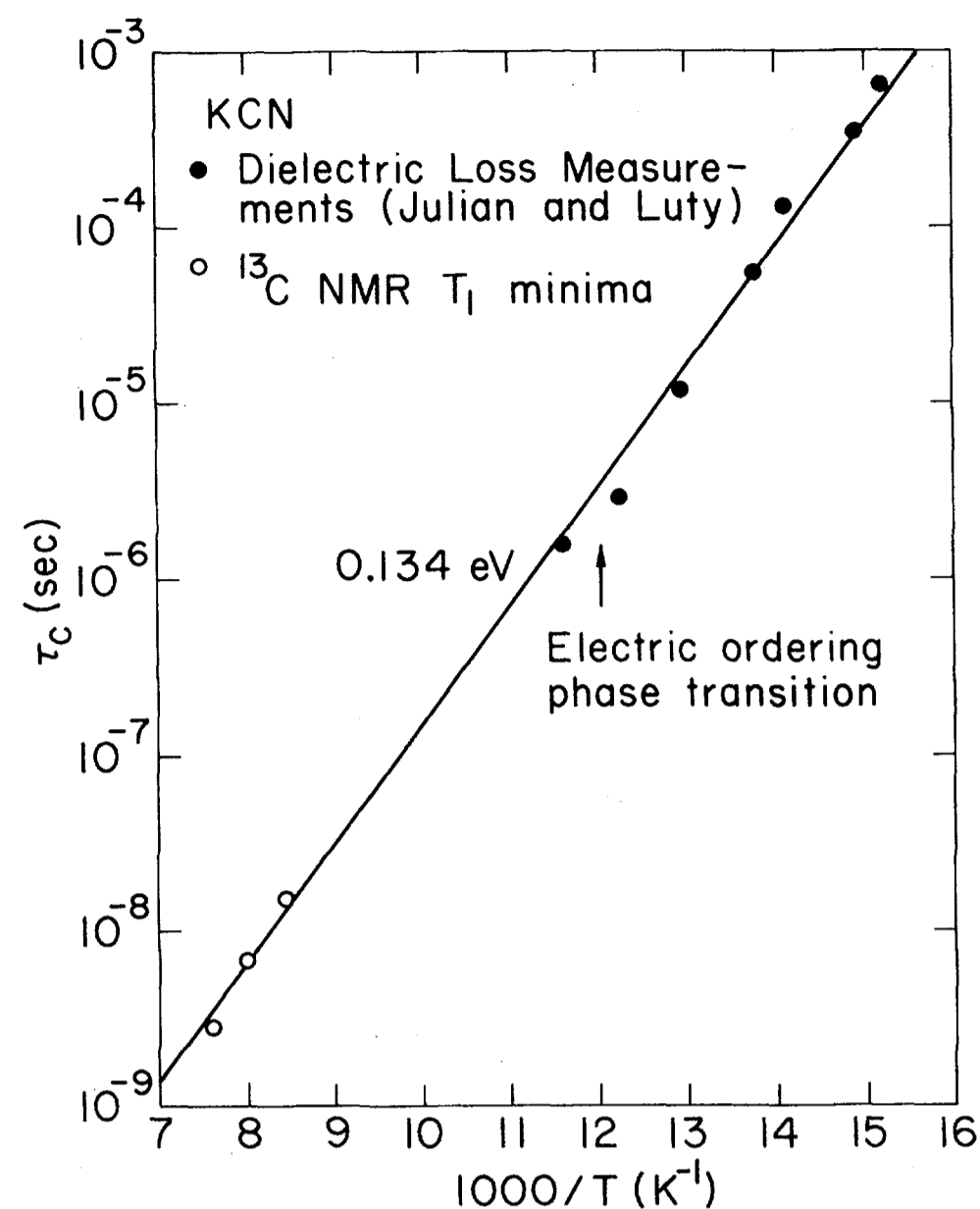


FIG. 3. Correlation time τ_c of the CN^- reorientations in KCN. The data obtained from dielectric loss measurements are from Refs. 4 and 11. The solid line is the least-squares fit of the data with a straight line.

electrically ordered phase, CN^- molecules still reorient head to tail, but now with a preferred direction. We see in Fig. 3 that this motion can be described by the same values of E_A and τ_0 on both sides of the phase transition. Thus, it is clear that the same motional mechanism is responsible for the relaxation in both the electrically ordered and electrically disordered phases. We have also observed this phenomenon in NaCN. More details will be presented in a later paper.

Using the values of E_A and τ_0 obtained from Fig. 3, we fitted T_1 data with Eq. (1) [using Eqs. (2), (3), and (6)], adding on an additional term due to relaxation from other sources (e.g., paramagnetic impurities) which limits T_1 at low temperature. (The form we use for this "background" relaxation is rather arbitrary and does not affect the results greatly.) From a least-squares fit (the solid lines in Fig. 2) we obtain $\alpha_{\text{rms}} = 2.30 \pm 0.6^\circ$. Thus, we can conclude from our NMR data that the CN^- molecules in KCN are misoriented on the average by about 2° .

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Observation of Anisotropy in the Temperature Dependence of the Positron-Annihilation Spectrum from a Single Crystal of Cadmium

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Measurements have been made on the Doppler broadening of the 511-keV photons resulting from positron annihilation in a single cadmium crystal over the temperature range 4–590 K. They show that the temperature dependence in the prevacancy region (150–350 K) is markedly different in the cases of emission in the [0001] and [10 $\bar{1}$ 0] directions.

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Positrons provide a sensitive probe of electronic conditions within a metal. Prior to annihilation they rapidly thermalize and a fraction of them may become trapped in defects such as vacancies, dislocations, etc. Measurements of the Doppler-broadening parameters of the annihilation 511-keV radiation can be used in conjunction with the trapping model^{1,2} to assess the thermal creation of vacancies and to estimate their concentrations, formation energies, and entropies, etc. Unfortunately, an unresolved problem casts doubt on the precision of these estimates: the marked temperature dependence of the parameters observed in the temperature region below the threshold of vacancy creation. In this so-called prevacancy region the physics is not understood and hence it is uncertain how the effect should be extrapolated into the vacancy region.

The most striking case is cadmium. Lichtenberger, Schulte, and MacKenzie³ found a steep increase in the Doppler line-height parameter between 180 and 350 K. Similar prevacancy rises in annealed samples have been seen in angular correlation measurements⁴ and in lifetime experiments.⁵ Our own group has reported Doppler-broadening measurements on both polycrystalline⁶

and single crystal⁷ specimens of cadmium, and it was differences between the results of the two cases that prompted the present study.

The most generally accepted explanation for the prevacancy rise has been recently enunciated by Stott and West.⁸ Taking into account volume thermal expansion and lattice vibrations, they propose that the reduction with increasing temperature in the overlap between positron and core electron wave functions might account for the observations. An alternative view by Seeger⁹ based on the possibility of positrons being self-trapped in metastable states has not been confirmed experimentally—but neither has it been entirely ruled out.^{7,10}

In this Letter we report the first measurements on the directional dependence of the prevacancy characteristics. A number of specimens were cut from a 99.999%-pure single crystal of cadmium, and the crystallographic axes were determined. The measurements reported here refer to one sample comprised of two elements sandwiching 80 μ Ci of ²²NaCl. Each element had been spark cut, spark planed, and chemically polished; had a final diameter of 18 mm and thickness of 2 mm; and had been annealed at $< 10^{-6}$ Torr for 6