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Model for CN^- reorientations in the low-temperature phases of KCN and NaCN

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We present a simple model for the CN^- reorientations in the low-temperature phases of KCN and NaCN. Our model predicts a small change in activation energy as the crystals go through the phase transition to the antiferroelectric state. We compare our results with experimental data.

I. INTRODUCTION

KCN and NaCN both undergo a low-temperature order-disorder phase transition to an antiferroelectric state.[1,2] This phase transition is continuous and occurs at a temperature $T_c = 83$ K in KCN and 172 K in NaCN. (This phase transition is not to be confused with the discontinuous phase transition which occurs at 168 K in KCN and 288 K in NaCN.) Above T_c, the crystal structure is body-centered orthorhombic, and the CN^- ions are aligned along the orthorhombic b axis. However, the CN^- ions are *disordered* with respect to their C and N ends, and the ions are rapidly reorienting head to tail. Below T_c, the CN^- ions become ordered in an antiferroelectric manner as shown in Fig. 1. In this phase, the head-to-tail reorientations of the CN^- ions are still present, but occur at a much lower rate.

The average time τ between the reorientations of a CN^- ion in KCN and NaCN has been experimentally measured over eleven decades of value using NMR,[3-5] dielectric,[6,7] and ionic-thermal-conductivity[7] (ITC) techniques. The data seem to indicate,[3,7] to within experimental accuracy, that τ follows an Arrhenius relation with the *same* activation energy and attempt frequency on *both* sides of the transition at T_c. However, we can see from physical arguments that the dynamic behavior of the ions cannot *really* be the same in both phases. In the ordered phase, each CN^- ion has a "preferred" orientation and spends most of its time oriented in that direction. Any reorientation of a CN^- ion from its preferred direction is quickly followed by another reorientation to bring it back to its preferred direction. In the disordered phase, there are no preferred orientations, and the CN^- ion spends an equal amount of time, on the average, oriented in each direction. The dynamic behavior of the CN^- ions is *different* in the two phases, and we would expect this difference to be *somehow* reflected in the reorientation time τ.

In this paper a simple model for CN^- reorientations is presented. This model predicts a small change in activation energy as either KCN or NaCN passes through the phase transition. We illustrate this result by a Monte Carlo computer simulation of the reorientations using an Ising model. We also examine experimental evidence supporting our model.

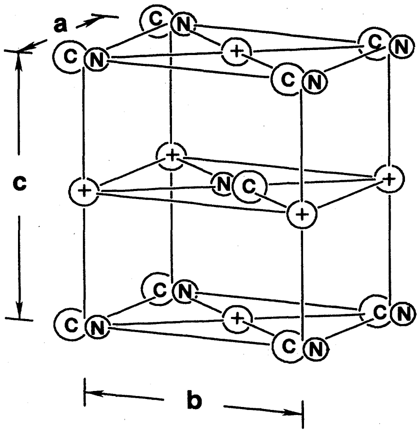

FIg. 1. Structure of KCN and NaCN in the antiferroelectric phase ($T > T_c$). Ions marked + are the K^+ or Na^+ ions.

II. MODEL FOR REORIENTATIONS

In this section, we present a simple model for CN^- reorientations in KCN and NaCN. We assume that every CN^- ion has only two possible orientations, $\theta = 0$ and $\theta = \pi$, where θ is the angle between the C-N axis and the orthorhombic b axis. Consider, first of all, a CN^- ion which may be oriented in either direction with equal probability. This means that the energy of this CN^- is the same, on the average, for both orientations. Between the two orientations, there is an energy barrier of height E_A, called the activation energy (Fig. 2). We assume that the

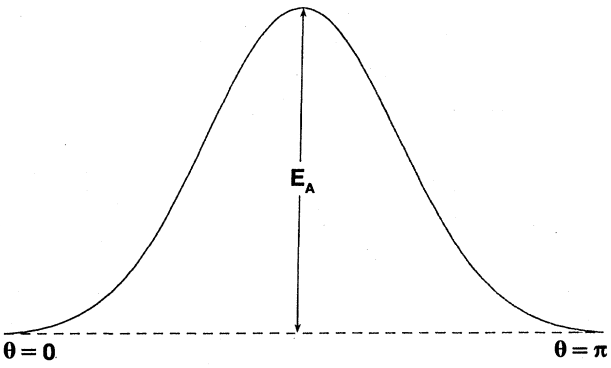

FIG. 2. The two orientations of a CN^- ion separated by an energy barrier. The two orientations are equally probable.

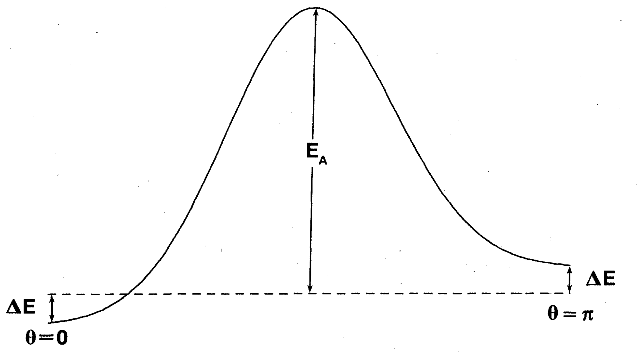

FIG. 3. The two orientations of a CN$^-$ ion separated by an energy barrier. The orientation at $\theta=0$ is preferred over the orientation at $\theta=\pi$.

average time τ between reorientations follows on Arrhenius relation,

$$\tau=\tau_0\exp(E_A/k_BT)\ , \tag{1}$$

where k_B is Boltzmann's constant, T is the temperature, and $1/\tau_0$ is called the attempt frequency.

In general, there are interactions present which can lower or raise the CN$^-$ energy in either of the two orientations. In the disordered phase (above T_c), we assume that these interactions average to zero so that τ is given by Eq. (1). In the ordered phase (below T_c), one orientation is energetically preferred over the other. We put this feature into the model by *lowering* the energy of the preferred orientation (call it $\theta=0$) by an amount ΔE and *raising* the energy of the other orientation ($\theta=\pi$) by the same amount ΔE (Fig. 3). The energy barrier for a reorientation from $\theta=0$ to π is now $E_A+\Delta E$, and the energy barrier for a reorientation from $\theta=\pi$ to 0 is $E_A-\Delta E$. Substituting these values of the energy barrier for E_A in Eq. (1), we see that the average reorientation time τ is different for these two kinds of reorientations. The average value of τ for *both* kinds of reorientations is given by

$$\tau=\tfrac{1}{2}\tau_0\exp\left[\frac{E_A+\Delta E}{k_BT}\right]+\tfrac{1}{2}\tau_0\exp\left[\frac{E_A-\Delta E}{k_BT}\right]\ . \tag{2}$$

At very low temperatures, the first term in Eq. (2) dominates τ, and the effective activation energy is greater than E_A by the amount ΔE. At temperatures just below T_c, the CN$^-$ ions are only partially ordered (the transition is continuous), and τ should have some value between the two values of Eqs. (1) and (2).

III. MONTE CARLO SIMULATION

The results of the model presented in Sec. II were verified with a Monte Carlo computer simulation. We used the Ising model in this simulation, even though it has been shown[8,9] that the Ising model does not give a good representation of the interactions between CN$^-$ ions in KCN and NaCN. However, the Ising model is mathematically simple, and the simulations carried out here are probably not very model dependent.

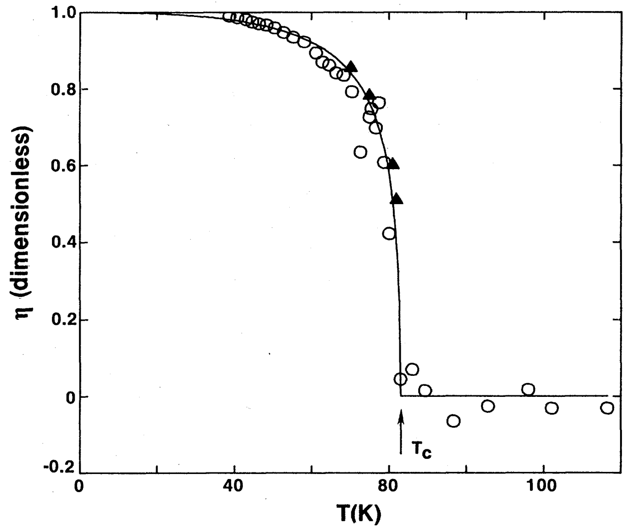

FIG. 4. Order parameter η in KCN. Circles are from our Monte Carlo simulation. Triangles are from neutron-diffraction data of Rowe, Rush, and Price (Ref. 1).

Consider two CN$^-$ ions, labeled i and j. In the Ising model the energy of interaction between these two ions is given by $E_{ij}=-J_{ij}S_iS_j$, where J_{ij} is the coupling parameter, and S_i and S_j are equal to ±1, depending on the orientation of each CN$^-$ ion. We will assume that only nearest-neighbor CN$^-$ ions interact, so that all J_{ij} are zero, except when ions i and j are nearest neighbors. By symmetry, all coupling parameters J_{ij} for nearest neighbors must be equal to the same value (call it J). Since in the antiferroelectric phase all nearest-neighbor pairs of CN$^-$ ions are antiparallel ($S_i=-S_j$), the value of J must be negative. The energy of interaction between a single CN$^-$ ion (labeled i) and its eight nearest neighbors (labeled j) is given by

$$E_i=\left[-J\sum_j S_j\right]S_i\ . \tag{3}$$

This model is identical to the Ising model for the body-centered-cubic lattice, which has been extensively studied. The ordering phase transition occurs at $k_BT_c=(6.35)|J|$ (see Ref. 10), so that $J=-1.13$ meV in KCN and -2.34 meV in NaCN.

When the CN$^-$ ions are completely ordered in the antiferroelectric phase, all nearest-neighbor pairs are antiparallel to each other, so that $S_j=-S_i$ in Eq. (3) and the energy is $E_i=-8|J|$. If the CN$^-$ ion reorients ($S_i\rightarrow-S_i$), then $E_i=+8|J|$. From Fig. 3, we can thus identify the quantity $\Delta E=8|J|$.

The order parameter η is defined to be

$$\eta=\frac{1}{N}\sum_i S_iS_i^{(0)}\ , \tag{4}$$

where N is the number of CN$^-$ ions in the crystal, and

$S_i^{(0)}$ is the orientation of the ith ion when the crystal is completely ordered. The value of $S_i^{(0)}$ is equal to $+1$ for half of the ions in the crystal and equal to -1 for the other half. The summation in Eq. (4) is taken over all CN$^-$ ions in the crystal. We see that $\eta = 0$ when the CN$^-$ ions are completely disordered, and $\eta = 1$ when they are completely ordered.

The Monte Carlo simulation was carried out using 1024 CN$^-$ ions arranged in a body-centered configuration. We used periodic boundary conditions so that the crystal had no surfaces. An equilibrium state, at any given T, was obtained in the usual manner. Some initial orientation was chosen for each CN$^-$ ion. For each CN$^-$ ion, the energy E_i was calculated from Eq. (3) for both of its possible orientations, $S_i = \pm 1$, and then its new orientation was chosen from a random distribution weighted in favor of the lowest value of E_i by the Boltzmann factor. This procedure was repeated 500 times over the entire crystal.

After obtaining the equilibrium state at each value of T, the order parameter η was calculated using Eq. (4). We plot the results for KCN in Fig. 4 (open circles). Rowe, Rush, and Prince[1] have obtained experimental values of η in KCN from neutron-diffraction data at four different temperatures. These values are plotted as solid triangles in Fig. 4 and are in good agreement with our computer-simulated data. The data for $T < T_c$ are well represented by the function

$$\eta = \exp[-A \ln^2(1 - T/T_c)] \;, \tag{5}$$

where A is a constant equal to 0.05 (determined by a best fit to the data). We plot Eq. (5) as a solid line in Fig. 4. This relation is only empirical, and we use it only as a convenient mathematical representation of η in subsequent figures.

Once the equilibrium state was obtained, the CN$^-$ reorientations were simulated. For each ion S_i, the energy barrier for reorientation was taken to be equal to $E_A - E_i$. The time at which each ion would reorient was randomly chosen from an exponential distribution of values that have an average equal to

$$\tau_i = \tau_0 \exp[(E_A - E_i)/k_B T] \;.$$

Each CN$^-$ ion was then reoriented at the time thus chosen. After each reorientation of an ion, a new time for the next reorientation of that ion was calculated. Also, the time for reorientation for each of the eight nearest-neighbor ions was recalculated since their energies E_j were changed by the reorientation of the ion at i. We carried out the computer simulation for 2000 reorientations in the crystal.

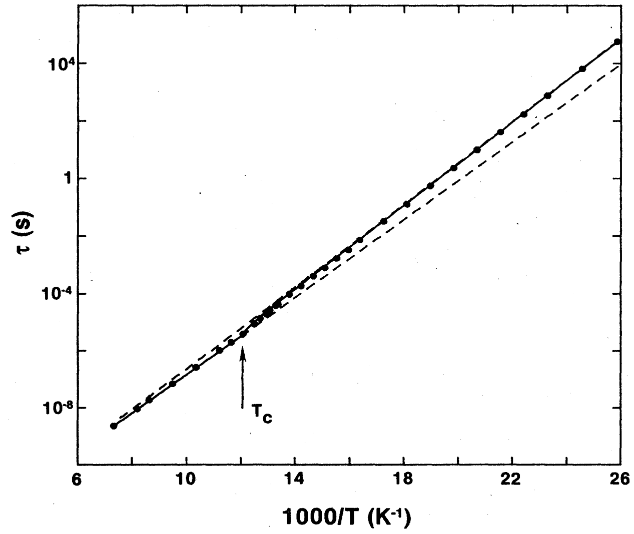

FIG. 5. Reorientation time τ in KCN. Points are from our Monte Carlo simulation.

From this simulation we obtained a value for the average time τ between reorientations of a CN$^-$ ion in KCN. These are plotted in Fig. 5. (We used $E_A = 0.134$ eV and $\tau_0 = 2.6 \times 10^{-14}$ s from Ref. 3.) The two expressions for τ in Eqs. (1) and (2) are drawn as dashed lines in the figure. As can be seen, the values of τ from our computer simulation clearly obey Eq. (1) above T_c and Eq. (2) below T_c. From a close examination of our data, we found that a good empirical expression for τ is given by

$$\tau = \eta \tau_{\rm lo} + (1 - \eta) \tau_{\rm hi} \;, \tag{6}$$

where $\tau_{\rm lo}$ is the low-temperature limit of τ given by Eq. (2) and $\tau_{\rm hi}$ is the high-temperature limit given by Eq. (1). We plot Eq. (6) as a solid line in Fig. 5.

IV. COMPARISON WITH EXPERIMENTAL DATA

We plot in Fig. 6 experimental values of τ in KCN obtained from NMR data of Stokes, Ailion, and Case,[3] and dielectric and ITC data of Lüty and Ortiz-Lopez.[7] From a best fit of Eq. (6) to this data (the solid line), we obtained $E_A = 0.1434$ eV and $\tau_0 = 1.10 \times 10^{-14}$ s. Above T_c, the slope of the line is just E_A. The dashed line is a continuation of this line on the other side of the phase transi-

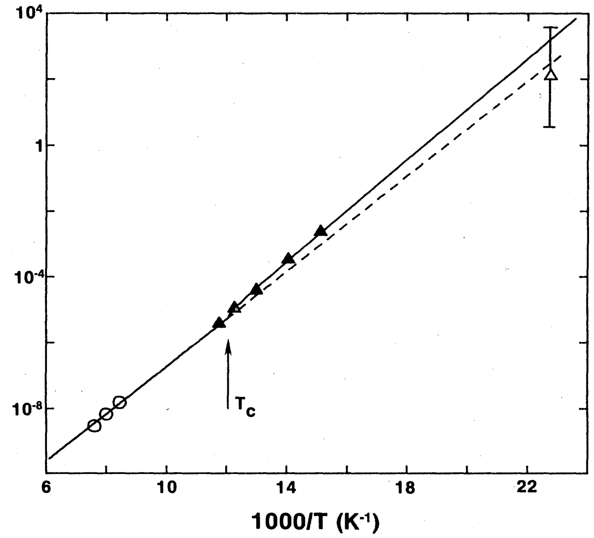

FIG. 6. Reorientation time τ in KCN. ○, NMR data from Stokes, Ailion, and Case (Ref. 3). ▲, dielectric response data; △, ITC data of Lüty and Ortiz-Lopez (Ref. 7). Solid line is the best fit of Eq. (6).

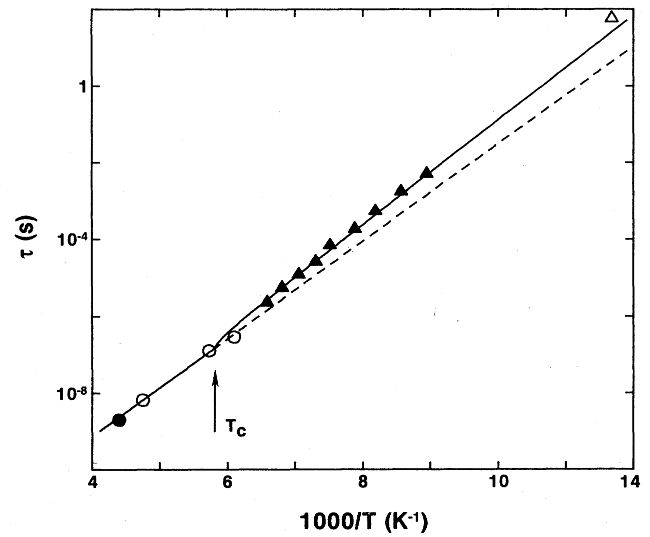

FIG. 7. Reorientation time τ in NaCN. ●, NMR data from Buchheit *et al.* (Ref. 4); ○, NMR data from Stokes, Ailion, and Case, (Ref. 3); ▲, dielectric response data; △, ITC data of Lüty and Ortiz-Lopez (Ref. 7). Solid line is the best fit of Eq. (6).

tion. Below T_c, the slope of the line is

$$E_A+\Delta E=E_A+8\,|J\,|=0.1524 \text{ eV} .$$

As can be seen, our model fits the data satisfactorily. However, the data could be fitted just as well by a single straight line through both phases. The data are consistent with our model but do not *verify* it.

We also simulated CN^- reorientations in NaCN and obtained results very similar to KCN. We plot in Fig. 7 experimental values of τ in NaCN obtained from NMR data of Stokes, Ailion, and Case,[3] NMR data of Buchheit *et al.*,[4] and dielectric and ITC data of Lüty and Ortiz-Lopez.[7] From a best fit of Eq. (6) to this data (the solid line), we obtained $E_A=0.2521$ eV and $\tau_0=6.10\times10^{-15}$ s. Below T_c, the slope of the line is 0.2708 eV. As with KCN, the data are consistent with our model but do not *verify* it.

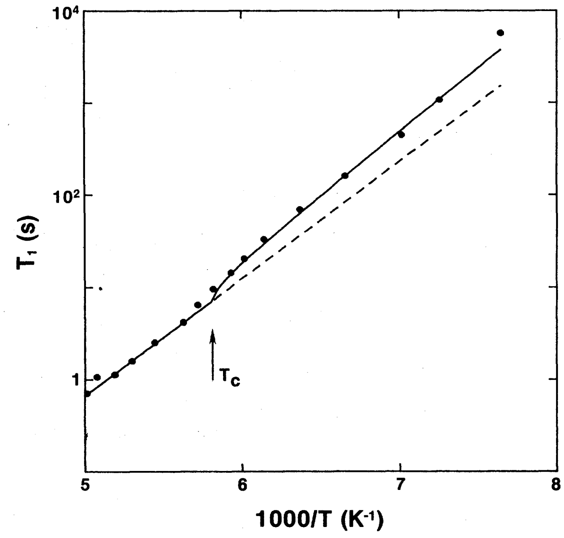

FIG. 9. ^{23}Na NMR T_1 data at 18.2 MHz from Elschner and Petersson (Ref. 5).

More convincing evidence for our model can be found in NMR relaxation data for NaCN. Reorientations of the CN^- ions cause fluctuations in the ^{23}Na nuclear-quadrupole interactions, leading to spin-lattice relaxation. Using an NMR frequency ω, the relaxation time T_1 for this process has a minimum value near the temperature where $\omega\tau=1$. At lower temperatures, T_1 is proportional to τ.

In Figs. 8—10 we show three different sets of T_1 data

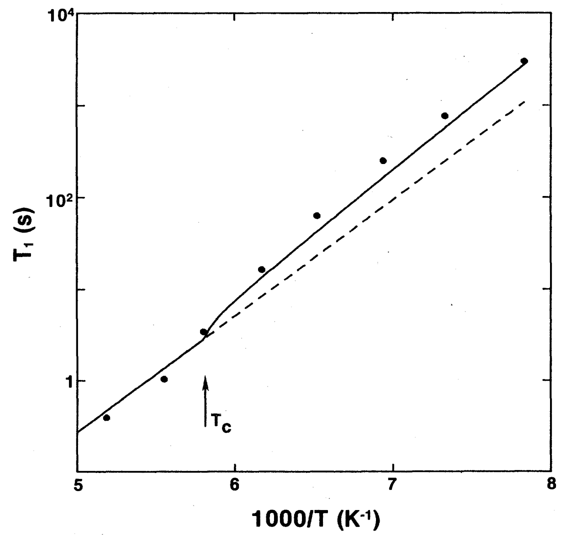

FIG. 8. ^{23}Na NMR T_1 data at 24 MHz from Stokes, Ailion, and Case (Ref. 3).

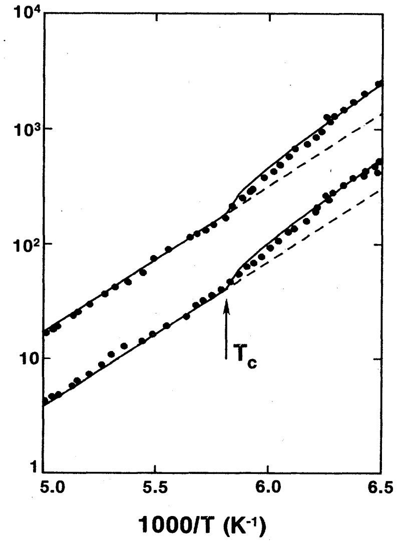

FIG. 10. ^{23}Na NMR T_1 data at 79.4 MHz from Buchheit *et al.* (Ref. 4).

(from Stokes, Ailion, and Case,[3] Elschner and Petersson,[5] and Buchheit *et al.*,[4] respectively). Note that the raw T_1 data include relaxation due to paramagnetic impurities which affects the data at low temperatures. We subtracted off this background relaxation to obtain the data points in Figs. 8—10.

The solid line in each of these three figures is simply the solid line shown in Fig, 7, multiplied by a constant (chosen to give a best fit to the data). The slopes of these lines were determined by a best fit to the data in Fig. 7 and are *not* adjustable parameters in Figs. 8—10. The agreement between the data and the results of our model is evident. The two regions of different slope below and above T_c are particularly clear in the data in Figs. 9 and 10. These data constitute strong evidence in favor of our model for CN$^-$ reorientations in KCN and NaCN.

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