

## Nuclear-Magnetic-Resonance Determination of Structural Domains in NaCN

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Measurements of the first- and second-order quadrupole energy-level shifts are performed in a  $^{23}\text{Na}$  NMR experiment in a single crystal of NaCN. Twelve orthorhombic domains are found below the phase transition at  $15^\circ\text{C}$ . They consist of six pairs of domains with each one oriented by an angle  $2\beta$  relative to the other member of the pair. The angle is around the  $c$  orthorhombic axis which coincides with the cubic  $[100]$  direction of the room-temperature pseudocubic phase. The angle  $\beta$  is found to be  $\pm(8.5^\circ \pm 1.5^\circ)$  at  $247^\circ\text{K}$ .

The study of domain crystallography of a multidomain crystal has been a topic of considerable interest.<sup>1-7</sup> In this paper, nuclear magnetic resonance is used to unravel relative orientations of domain in a multidomain crystal. The measurement of the angular dependence of the  $^{23}\text{Na}$  nuclear energy levels, shifted by quadrupole interactions, makes possible the unambiguous determination of the domain orientation with respect to the cubic phase of NaCN as well as between each other.

The room-temperature phase of NaCN is a pseudocubic (NaCl-type) structure with orientational disorder of the CN group. A sharp first-order phase transition is observed at  $288^\circ\text{K}$ . An ordering of the CN group occurs which is approximately along the  $[110]$  cubic directions. The transparent single crystal breaks up in a multidomain structure of orthorhombic domains and becomes opaque. From space-group considerations<sup>5</sup> the possible number of domains are 6, 8, and 12. X-ray investigations<sup>4-7</sup> of KCN shows that one can have two possible domain configurations. In Ref. 4 there is a model which offers a detailed description of the formation of twelve domains. In this model the cubic unit cell is distorted by an angle  $2\beta$  to form a monoclinic cell in which the orthorhombic one is incorporated. A second possible configuration consists of eight domains which are observed in a constrained<sup>4-7</sup> KCN crys-

tal. The domain structure of NaCN has not been investigated thoroughly but is usually assumed to be similar to KCN. In the orthorhombic phase the head-to-tail flip of the  $\text{CN}^-$  group has been established.<sup>8</sup> Table I summarizes the x-ray and neutron diffraction<sup>9,10</sup> measurements of the  $a$ ,  $b$ , and  $c$  orthorhombic unit-cell lengths as well as the angle of distortion  $\beta$ , described in Refs. 4 and 6.

The Hamiltonian of  $^{23}\text{Na}$  is composed of Zeeman and quadrupolar parts,

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_Q. \quad (1)$$

TABLE I. NaCN orthorhombic unit-cell dimensions in different temperatures and the corresponding angle  $\beta$  calculated from  $\beta = \frac{1}{4}\pi - \tan^{-1}(a/b)$  (Ref. 6).

Temperature ( $^\circ\text{K}$ )	$a$ ( $\text{\AA}$ )	$b$ ( $\text{\AA}$ )	$c$ ( $\text{\AA}$ )	$\beta$ (deg)	Ref.
4.2	3.63	4.85	5.45	8.2	9
$\sim 143$	3.70	4.77	5.56	7.2	1
180	3.69	4.80	5.57	7.5	10
$\sim 263$	3.75	4.72	5.62	6.5	1

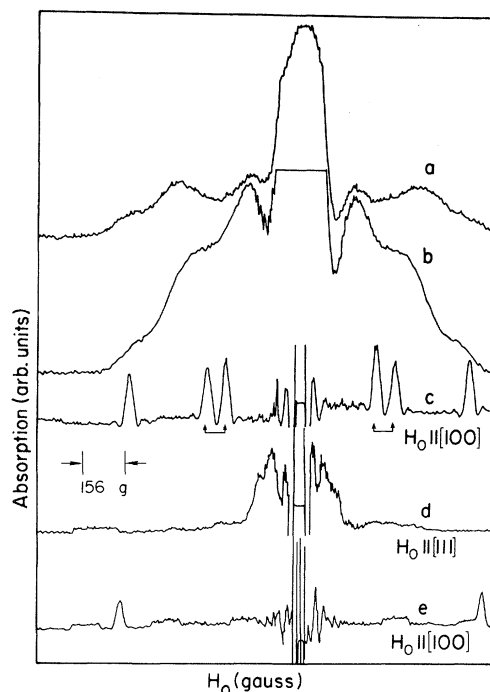


FIG. 1. Curve  $a$ , powder pattern at  $191^\circ\text{K}$ ; curve  $b$ , powder pattern at  $247^\circ\text{K}$ ; curves  $c$ - $e$  show satellite ( $\pm\frac{1}{2}$  to  $\pm\frac{3}{2}$ ) transitions in a single crystal: curve  $c$ ,  $\vec{H}_0 \parallel [100]$  at  $247^\circ\text{K}$ ; curve  $d$ ,  $\vec{H}_0 \parallel [111]$  at  $247^\circ\text{K}$ ; and curve  $e$ ,  $\vec{H}_0 \parallel [100]$  at  $191^\circ\text{K}$ .

Since the experiment was performed at the Larmor frequency 24 MHz and the quadrupole interaction is of order 1 MHz,<sup>11</sup> the latter is considered as a perturbation on the Zeeman interaction. Figure 1, curves *a* and *b* show the powder pattern of <sup>23</sup>Na. On each side of the central (-½ to +½) transition three peaks are observed.<sup>12</sup> They are shifted by Δν<sub>1</sub>, Δν<sub>2</sub>, and Δν<sub>3</sub> from the center of the powder pattern. The strength of the quadrupole interaction and the asymmetry parameter are given by<sup>12</sup>

$$e^2qQ/h = 2(\Delta\nu_1 + \Delta\nu_2) = 2\Delta\nu_3 \quad (2a)$$

and

$$\eta = (\Delta\nu_2 - \Delta\nu_1)/(\Delta\nu_1 + \Delta\nu_2). \quad (2b)$$

The quadrupole frequency for  $I = \frac{3}{2}$  (<sup>23</sup>Na) is given

$$\Delta\nu_{1/2 \rightarrow -1/2}^{(2)} = \frac{\nu_Q^2}{12\nu_L} \left[ -\frac{9}{4} \sin^2\theta (9 \cos^2\theta - 1) - \frac{3}{2} \eta \cos 2\varphi \sin^2\theta (9 \cos^2\theta + 1) + \eta^2 \left( \frac{9}{4} \cos^2 2\varphi \sin^4\theta + 3 \cos^2\theta - 2 \right) \right], \quad (4)$$

where θ and φ are the first two Euler angles for the transformation from the system of the principal axes of the electric-field-gradient tensor to a laboratory system in which the external-magnetic-field direction becomes the new z direction. The satellite (±½ to ±½) transitions are affected mainly by first-order perturbation shifts<sup>14</sup>:

$$\Delta\nu_{+3/2 \rightarrow +1/2}^{(1)} = -\Delta\nu_{-1/2 \rightarrow -3/2}^{(1)} = \nu_Q (3 \cos^2\theta - 1 - \frac{1}{2} \eta \cos 2\varphi \sin^2\theta). \quad (5)$$

Figure 1, curve *d* shows that the satellite transitions collapse into almost one line for the magnetic field  $\vec{H}_0 \parallel [111]$  cubic direction, which suggests that the [100] cubic direction is the main axis of the quadrupole interaction. Two single crystals of NaCN were studied: In one the magnetic field was rotated in the (110) plane, while in the second the magnetic field was rotated in the (100) plane. The spectra for the central transition (Fig. 2) and the satellite transitions (Fig. 1, curves *c-e*) were ob-

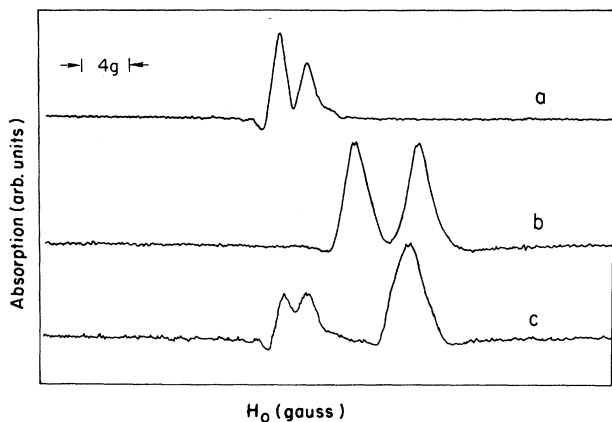


FIG. 2. The central (-½ to +½) transition for three orientations of the magnetic field: curve *a*,  $\vec{H}_0 \parallel [100]$ ; curve *b*,  $\vec{H}_0 \parallel [111]$ ; and curve *c*,  $\vec{H}_0 \parallel [110]$ .

by<sup>13</sup>

$$\nu_Q = (e^2qQ/2h)(1 + \frac{1}{3}\eta^2)^{1/2}. \quad (3)$$

A measurement of the spin-lattice relaxation time  $T_1$  as a function of the temperature exhibits a typical Bloembergen-Purcell-Pound behavior. The minimum is due to the 180° flips of the CN<sup>-</sup> groups and occurs at about 203 °K. At 191 °K ( $\omega_L \tau \gg 1$ , where  $\omega_L$  is the Larmor frequency and  $\tau$  is the correlation time for 180° flips for CN<sup>-</sup>)  $e^2qQ/h = 1456 \pm 30$  kHz and  $\eta = 0.42 \pm 0.02$ . At 247 °K ( $\omega_L \tau \ll 1$ )  $e^2qQ/h = 1396 \pm 30$  kHz and  $\eta = 0.375 \pm 0.02$ .

The determination of the direction of the electric-field-gradient tensor is done by observing in a single crystal the angular dependence of the central (-½ to +½) transition (Fig. 2) and the satellite (±½ to ±½) transitions (Fig. 1, curves *c-e*). The central transition is affected only by the second-order shift of the energy levels<sup>14</sup>:

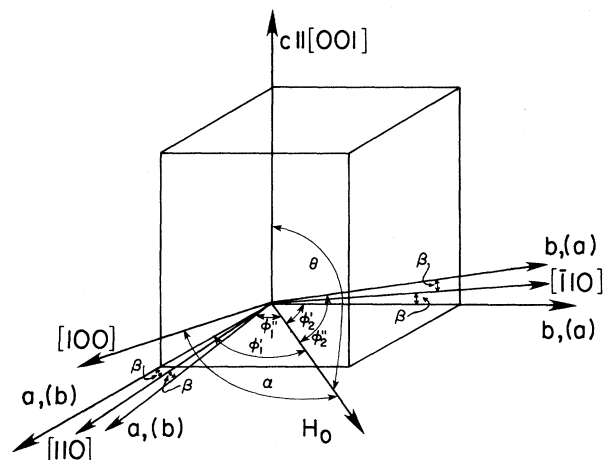


FIG. 3. Two pairs of domains are shown ( $\theta = \theta_1' = \theta_1'' = \theta_2' = \theta_2''$ ).

tained separately since they have different linewidths.

In order to analyze the NMR spectra, one has to calculate the set of the first two Euler angles  $\theta$  and  $\varphi$  (as defined in Ref. 14 and Fig. 3) as a

$$\begin{aligned} \theta_1' = \theta_1'' = \alpha, \quad \varphi_1' = -(\frac{1}{4}\pi - \beta), \quad \varphi_1'' = -(\frac{1}{4}\pi + \beta); \quad \theta_2' = \theta_2'' = \alpha, \quad \varphi_2' = \frac{1}{4}\pi + \beta, \quad \varphi_2'' = \frac{1}{4}\pi - \beta; \\ \theta_3' = \theta_3'' = \frac{1}{2}\pi, \quad \varphi_3' = \frac{1}{4}\pi - \beta + \alpha, \quad \varphi_3'' = \frac{1}{4}\pi + \beta + \alpha; \quad \theta_4' = \theta_4'' = \frac{1}{2}\pi, \quad \varphi_4' = \frac{1}{4}\pi + \beta - \alpha, \quad \varphi_4'' = \frac{1}{4}\pi - \beta - \alpha; \quad (6) \\ \theta_5' = \theta_5'' = \frac{1}{2}\pi - \alpha, \quad \varphi_5' = \frac{3}{4}\pi + \beta, \quad \varphi_5'' = \frac{3}{4}\pi - \beta; \quad \theta_6' = \theta_6'' = \frac{1}{2}\pi - \alpha, \quad \varphi_6' = \frac{1}{4}\pi - \beta, \quad \varphi_6'' = \frac{1}{4}\pi + \beta. \end{aligned}$$

In the above equation, the ' and '' superscripts refer to angles  $\theta$  and  $\varphi$  for the two different domains of a pair, whose relative angle is  $2\beta$ . The subscripts 1-6 refer to the six different pairs of domains. For the crystal where the magnetic field is rotated in the (110) plane, the reference direction is again the cubic [100] and  $\alpha$  is the angle between the magnetic field and the reference direction.

Let us discuss first the angular dependence of the central transition. Figure 2 shows the spectra for  $\vec{H}_0$  parallel to the three cubic directions [100], [110], and [111]. The magnetic field is rotated through all three directions for the (110)-oriented crystal. For the case  $\vec{H}_0 \parallel [100]$  ( $\alpha = 0$ ) one has  $\theta = 0$  (the terms involving  $\varphi$  drop out) for four domains, whereas  $\theta = 90^\circ$ ,  $\varphi \sim 45^\circ$  for the remaining eight domains ( $\varphi$  deviates from  $45^\circ$  by the angle  $\beta$ ). A calculation based on Eq. (4) shows that the splitting is within the linewidth. There are two lines (Fig. 2, curve *a*) whose intensity ratio is 2:1 and whose second-order shifts are 3.1 and 0.22 G in the low-field direction. For the case  $\vec{H}_0 \parallel [111]$  (Fig. 2, curve *b*) one has two lines with equal intensity. For this case,  $\alpha = 54.74^\circ = \theta_1 = \dots = \theta_6$  and  $\varphi$  is approximately zero for six of the domains and is approximately  $\frac{1}{2}\pi$  for the remaining six domains. The lines are shifted by  $-2.3$  and  $-7.0$  G.

For the case  $\vec{H}_0 \parallel [110]$  (Fig. 2, curve *c*), the result for  $\alpha = \frac{1}{4}\pi$  is a three-line pattern corresponding to two domains, two domains, and eight domains. For the intense line shifted by  $-6.3$  G one has  $\theta = 45^\circ$  and  $\varphi \sim 45^\circ$ . This is the most sensitive line for distinguishing between the six-domain model (where  $\beta = 0$ ) and the twelve-domain model. If there are twelve domains, this line should be split into two lines, in contrast to the six-domain case which has only one such line. However, the breadth of the line is sufficiently great that no splitting is observed.

We performed a calculation of the spectra us-

ing Eq. (4), in which the values for  $e^2qQ$  and  $\eta$  were determined from the powder pattern and satellite measurements (Fig. 1, curves *c* and *e*). We obtained excellent quantitative agreement between this calculated result and the experiment data shown in Fig. 2. The complete correspondence between the calculated spectra and the measured ones proves that the principal directions of the electric field gradient for  $^{23}\text{Na}$  are the three *c* orthorhombic axes coinciding with the three  $\langle 100 \rangle$  cubic directions. However, it is not possible from these data alone to decide whether one has six or twelve domains.

Let us discuss the spectra of the satellite transitions. Figure 1, curve *c* shows the spectrum for  $\vec{H}_0 \parallel [100]$ . This particular orientation is the most sensitive one for distinguishing between the six- and the twelve-domain models for measuring the relative angle  $2\beta$  between each pair of the six domains. The calculation of the first-order shifts is based on Eq. (5). As discussed earlier,  $\theta = \alpha = 0$  (no  $\varphi$  terms) for four domains and  $\theta = 90^\circ$ ,  $\varphi = 45^\circ \pm \beta$  for the other eight domains. However, a splitting is observed in the satellite line (indicated by arrows in Fig. 1, curve *c*). The spectrum has been fitted with  $\theta = 90^\circ$  and  $\varphi = 36.5^\circ, 53.5^\circ$  corresponding to  $\beta = \pm 8.5^\circ$ . Each of the three satellites corresponds to four domains. This is the crucial spectrum for distinguishing between six and twelve domains, since a six-domain spectrum would result in only two satellites rather than the three which we observe. The eight-domain model discussed in Refs. 4 and 6 is not present in our crystal. In this case there is only one *c* orthorhombic direction which coincides with one of the  $\langle 100 \rangle$  cubic directions. To rule out this possibility, the crystal oriented in a (100) plane was rotated by  $90^\circ$  from the [100] direction and an identical spectrum was found. If the eight-domain model were valid, this rotation should result in a different

spectrum.

In conclusion we have established the existence of twelve orthorhombic domains in NaCN. We have determined their relative orientation both to the pseudocubic phase and to each other.

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## Melting in Two Dimensions is First Order: An Isothermal-Isobaric Monte Carlo Study

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Isothermal-isobaric Monte Carlo computer experiments on melting in a two-dimensional Lennard-Jones system indicate that the transition is first order, in contrast to the two-stage, second-order melting behavior suggested as a possibility by Halperin and Nelson.

Expanding on the proposals by Kosterlitz and Thouless<sup>1</sup> and by Feynman,<sup>2,3</sup> Halperin and Nelson<sup>4,5</sup> have developed a detailed theory of dislocation-mediated melting for a two-dimensional "crystal." One important feature of the Halperin-Nelson theory is the possibility that the transition from two-dimensional solid to two-dimensional liquid takes place by *two second-order* transitions with increasing temperature. At some temperature  $T_m$ , dissociation of dislocation pairs gives rise to a second-order transition from a solid phase, with algebraic decay of translational order and long-range orientational order, to a "liquid-crystal" ("hexatic") phase, with exponential decay of translational order *but* algebraic decay of sixfold orientational order. At a higher temperature  $T_i > T_m$ , dissociation of dislocations into disclinations gives rise to another second-order phase transition from the hexatic phase to

the isotropic fluid phase. Halperin and Nelson do emphasize that this particular melting mechanism is only one possibility. They cannot rule out the possibility of a first-order melting transition.

Direct experimental verification of the Halperin-Nelson theory for two-dimensional melting is difficult because several possible mechanisms are involved in real systems which might conceivably influence the apparent order of the transition; e.g., epitaxy, second-layer promotion, and heterogeneity, as well as the details of the adatom and substrate interactions.<sup>5</sup> In order to circumvent the uncertainties and limitations of current laboratory experiments, Frenkel and McTague<sup>6</sup> performed a "computer experiment" on the well-defined model system of Lennard-Jones (L-J) 12:6 atoms constrained to remain two dimensional. They chose the molecular-dynamics