ence is $\langle\{S^+(-\vec{q}), [\mathcal{H}, S^-(\vec{q})]\}\rangle$, which can be found using Eq. (1) of this paper to go as q^2. This implies that there is no long-range order in two dimensions.

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PHYSICAL REVIEW B VOLUME 4, NUMBER 1 1 JULY 1971

Electric-Field-Induced Quadrupole Splittings of Li^7 Nuclear Magnetic Resonance in KCl: Li^+†

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(Received 8 February 1971)

The electric-field-induced quadrupole splitting of the nuclear magnetic resonance of the off-center impurity ion Li^7 has been observed in KCl: Li^+. Observations of the dependence of the quadrupole splitting upon applied electric field in the [110] direction and upon orientation of the dc magnetic field confirm the value of the quadrupole coupling constant determined by Alderman and Cotts as well as the ⟨111⟩ tunneling model for the Li ion.

Before the observation[1] of stress-induced quadrupole splitting of Li^7 NMR in KCl: Li^+, an unsuccessful attempt was made to observe the splittings induced by a static electric field. Since the completion of the stress experiment and in view of other experiments[2,3] which demonstrate the validity of the ⟨111⟩ tunneling model of Gomez, Bowen, and Krumhansl[4] (GBK), efforts to observe the electric-field-induced splitting were resumed. We have now observed this splitting in samples prepared with special care and annealed to keep internal strains to a minimum.

The functional form of the energy levels of the Li^+ ion in KCl with an electric field applied has been calculated by a number of authors.[2-6] The electric field term in the Hamiltonian is $\mathcal{H}_E = -\vec{\mu}\cdot\vec{E}_0$, where $\vec{\mu}$ is the electric dipole moment of the off-center Li^+ ion and $\vec{E}_0$ is the applied field. The most accurate measure of $\vec{\mu}$ and Δ, the level spacing of the ground-state multiplet, has been made by Herendeen and Silsbee who find, for Li^7, $\vec{\mu} = 5.6 \pm 0.2 \times 10^{-18}$ esu cm and $\Delta = 0.77 \pm 0.03$ cm^{-1}.

The expected value of the electric-field-induced quadrupole splitting is calculated using the same formalism given in Alderman and Cotts.[1] The average value of the electric-field-gradient (EFG) tensor in the crystal axis coordinate system is

$$\langle\overleftrightarrow{V}'\rangle = Z^{-1}\sum_\mu e^{-E_\mu/kT}\,V'_\mu\,, \qquad (1)$$

where

$$Z = \sum_\mu e^{-E_\mu/kT}\,,$$

$$\overleftrightarrow{V}'_\mu = \int \Psi^*_\mu(\vec{r})\,\overleftrightarrow{V}'(\vec{r})\,\Psi_\mu(\vec{r})\,d^3r\,,$$

and the $\Psi_\mu(\vec{r})$ are the exact eigenfunctions of the impurity-ion wave function in the presence of an electric field. The Ψ_μ can be expressed in terms of the basis state functions ψ_n of the ⟨111⟩ tunneling model of GBK:

$$\Psi_\mu = \sum_n c_{n\mu}\psi_n\,, \qquad (2)$$

where n is summed over the eight well sites. The EFG tensor $\overleftrightarrow{V}'(\vec{r})$ is the sum of well-site tensors V'_n which have been transformed to a common coordinate system, the crystal axes (x', y', z') shown in Fig. 1. As in other work, it is assumed that the ψ_n are highly localized on each well site and only the "edge" overlap integrals[4] are important in the ground-state multiplet. The experiment is done for only one direction of the applied field $\vec{E}_0$ parallel to the [110] direction. Solutions to the ⟨111⟩ tunneling model predict that at sufficiently low temperatures a nonzero $\langle\overleftrightarrow{V}'\rangle$ is predicted. In addition, the resulting quadrupole splittings depend upon the direction of $\vec{E}_0$ and the applied dc magnetic field used in the nuclear-magnetic-resonance (NMR) ex-

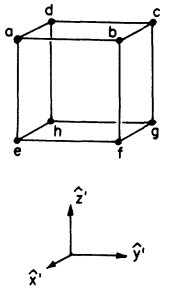

FIG. 1. Crystal axis coordinate system (x', y', z') and ⟨111⟩ potential well sites symmetrically located about vacant cation lattice site. Site labels are the same used by Gomez *et al.* in Ref. 4.

periment. $\vec{E} \parallel [110]$ and $\vec{E} \parallel [\bar{1}\bar{1}0]$ produce identical splittings. The E_n and Ψ_μ are obtained from the eigenvalue equation given by GBK:

$$\overleftrightarrow{H}\,\Psi = (E/\Delta)\,\overleftrightarrow{1}\,\Psi \ , \tag{3}$$

where $\overleftrightarrow{H}$ is

	A_{1g}	T_{1ux}	T_{1uy}	T_{1uz}	T_{2gxy}	T_{2gxz}	T_{2gyz}	A_{2u}
A_{1g}	$-\frac{3}{2}$	$P/\sqrt{2}$	$P/\sqrt{2}$	0	0	0	0	0
T_{1ux}	$P/\sqrt{2}$	$-\frac{1}{2}$	0	0	$P/\sqrt{2}$	0	0	0
T_{1uy}	$P/\sqrt{2}$	0	$-\frac{1}{2}$	0	$P/\sqrt{2}$	0	0	0
T_{1uz}	0	0	0	$-\frac{1}{2}$	0	$P/\sqrt{2}$	$P/\sqrt{2}$	0
T_{2gxy}	0	$P/\sqrt{2}$	$P/\sqrt{2}$	0	$\frac{1}{2}$	0	0	0
T_{2gxz}	0	0	0	$P/\sqrt{2}$	0	$\frac{1}{2}$	0	$P/\sqrt{2}$
T_{2gyz}	0	0	0	$P/\sqrt{2}$	0	0	$\frac{1}{2}$	$P/\sqrt{2}$
A_{2u}	0	0	0	0	0	$P/\sqrt{2}$	$P/\sqrt{2}$	$\frac{3}{2}$

and where $P = -\mu E_0/(\Delta\sqrt{3})$. Table I gives eigenvalues and eigenfunctions of the solution to Eq. (3). The energies are plotted in Fig. 2.

The EFG at each well site is axially symmetric. For example at the b site, the principal symmetry axis of tensor is parallel to $\langle 111 \rangle$. One parameter,[1] eq_0, is then needed to specify each EFG tensor once its principal axes are set by the well-site location. From the eigenfunctions Ψ_μ and use of Eq. (1), $\langle \overleftrightarrow{V}' \rangle$ is found, and in its principal-axis system it is

$$\langle \overleftrightarrow{V}' \rangle = N eq_0 \begin{pmatrix} 0 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \ . \tag{4}$$

The constant N is a function of temperature and applied field. $\langle \overleftrightarrow{V}' \rangle$ has an asymmetry parameter[1] $\eta = +1$. The principal axes (X, Y, Z) of $\langle \overleftrightarrow{V}' \rangle$ are in the directions ($[00\bar{1}]$, $[\bar{1}10]$, $[110]$) in terms of the coordinates (x', y', z').

The magnitude of the quadrupole splitting frequency for Li^7 which has spin $\frac{3}{2}$, quadrupole moment Q, is given by Eq. (5)[1]:

$$f_Q = (e^2Qq/h)(3\cos^2\theta - 1 + \eta \sin^2\theta \cos 2\phi) \ , \tag{5}$$

where $q = Nq_0$, θ, and ϕ are polar and aximuthal coordinates of the magnetic field direction in the principal-axis coordinate system. In this experiment with $\vec{E}_0 \parallel [110]$ and, for half of the crystal plates, $\vec{E}_0 \parallel [\bar{1}\bar{1}0]$, the direction of the magnetic field could be changed a limited amount in the (Y, Z) plane. Values of θ from 0 to $\frac{1}{4}\pi$ were available for one set of plates and correspondingly θ ranged from π to $\frac{5}{4}\pi$ in the other set. The direction $\theta = 0$ corresponds to [110]. The angle ϕ is fixed at 90° so that $\cos 2\phi = -1$, in which case we have

$$f_Q = \frac{e^2Qq_0N\cos 2\theta}{2h} \ , \tag{6}$$

and one pair of satellites is predicted.

The samples were cut from a KCl: Li^+ single crystal grown by the Cornell Materials Science Center, Crystal Growing Facility. The original

TABLE I. Energies and eigenvalues for $\vec{E}_0 \parallel [110]$.

Levels	Energies and eigenfunctions
$4_\pm$	$E_{4\pm} = \Delta[\frac{1}{2} \pm (1 + 2P^2)^{1/2}]$
	$\Psi_{4\pm} = C_\pm[T_{1uz} + \alpha_\pm T^+_{2g} + \beta_\pm A_{2u}]$
	$T^+_{2g} = (1/\sqrt{2})\,[T_{2gxz} + T_{2gyz}]$
	$C_\pm = \dfrac{P^2}{1 + 2P^2 \pm (1 + 2P^2)^{1/2}}$
	$\alpha_\pm = \dfrac{1 \pm (1 + 2P^2)^{1/2}}{P}$
	$\beta_\pm = \dfrac{1 + P^2 \pm (1 + 2P^2)^{1/2}}{P^2}$
$3_\pm$	$E_{3\pm} = \Delta[-\frac{1}{2} \pm (1 + 2P^2)^{1/2}]$
	$\Psi_{3\pm} = C_\pm[A_{1g} + \alpha_\pm T^+_{1u} + \beta_\pm T_{2gxy}]$
	$T^+_{1u} = (1/\sqrt{2})\,[T_{1ux} + T_{1uy}]$
$4_0, 2$	$E_{4_0} = E_2 = \Delta(\frac{1}{2})$
	$\Psi_{4_0} = [P/(1 + 2P^2)^{1/2}]\,[T_{1uz} + T^+_{2g}/P - A_{2u}]$
	$\Psi_2 = T^-_{2g} = (1/\sqrt{2})\,[T_{2gxz} - T_{2gyz}]$
$3_0, 1$	$E_{3_0} = E_1 = \Delta(-\frac{1}{2})$
	$\Psi_{3_0} = [P/(1 + 2P^2)^{1/2}]\,[A_{1g} + T^+_{1u}/P - T_{2gxy}]$
	$\Psi_1 = T^-_{1u} = (1/\sqrt{2})\,[T_{1ux} - T_{1uy}]$

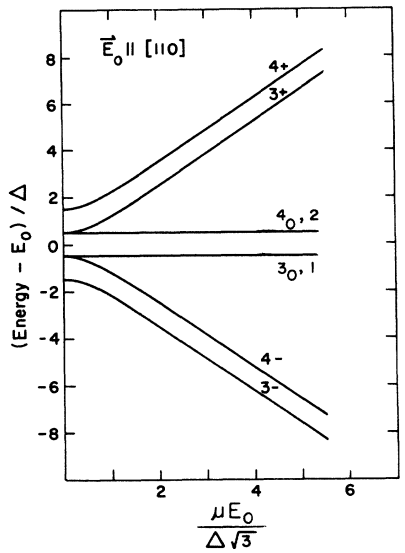

FIG. 2. Electric field dependence of energy levels. Maximum value of P used in this experiment equals about 3.9, corresponding to $E_0 = 55$ kV/cm.

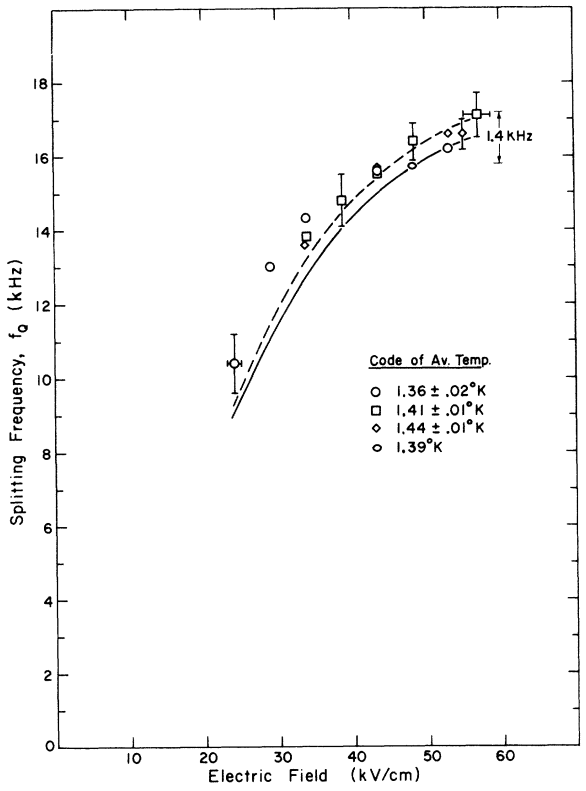

FIG. 3. Quadrupole splitting frequency dependence on electrical field. Solid curve is theoretical using Alderman's $e^2 Q q_0/h = 71$ kHz. Dashed curve is fit based on $e^2 Q q_0/h = 73.2$ kHz. Arrows indicate spread of uncertainty based upon the spread in error in Alderman's $e^2 Q q_0/h$ measurement.

melt contained 0.2% LiCl by weight. Lithium concentration near the region of the boule used was determined to be 8×10^{17} atoms/cm^3 by the Materials Science Center Chemical Analytic Facility.

Crystal plates approximately $1 \times 1 \times 0.1$ cm were cut with the [110] axis perpendicular to the large surfaces. The plates were mounted in a brass jig and sanded to a uniform thickness with emery abrasive paper. Final sample thickness was measured with a micrometer. The mean and mean-square deviation proved to be 0.098 ± 0.0015 cm. Eight KCl: Li^+ plates were stacked with copper sheets approximately 1×10^{-3} in. thick between the crystal plates. This stack was placed into a plastic holder and secured inside the rf coil with copper plates parallel to the direction of the oscillating rf field. Values of the electric field were calculated as the ratio of the potential difference maintained across the plates to the average plate thickness. Immediately prior to an experimental run the KCl: Li^+ samples were vacuum annealed in a quartz tube at 400 °C for at least 24 h with a 4-h cooling period to room temperature. Samples were mounted and cooled to 77 °K within 2 h of their removal from the annealing oven.

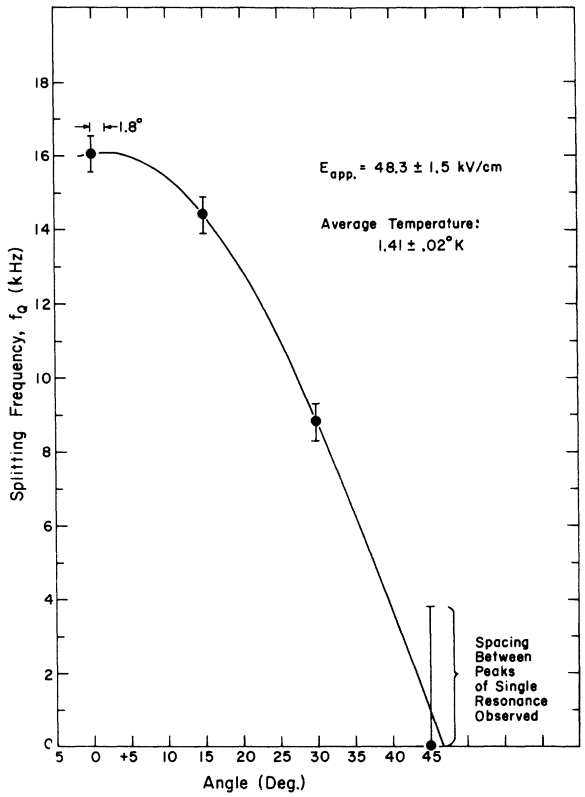

FIG. 4. Dependence of the splitting frequency upon direction θ of the magnetic field.

NMR spectra were recorded at 16 MHz using the twin-T bridge and a low-temperature amplifier developed and used by Alderman.[7] The cryostat was converted from stress field to electric field use. Data recorded consisted of (a) a study of the quadrupole splitting frequency versus electric field at $\theta = 0°$ and $T = 1.4$ °K and (b) a check of angular dependence of the splitting at θ equal to 15, 30, and 45° to the orientation in part (a) at a field of 48.3 $\pm$ 1.4 kV/cm. The angle θ was known to an uncertainty of $\pm 2°$. In view of the low signal-to-noise ratio, better alignment was not thought to be necessary. In the presence of $\vec{E}_0$, the signal-to-noise ratio of the satellite lines equals about 4 or 5 to 1.

Figure 3 shows measured quadrupole splitting versus applied electric field along [110] at temperatures near 1.4 °K. The solid line in this plot represents a theoretical calculation based upon Eq. (6) and (a) the previously determined[1] value of $e^2Qq_0/h = 71 \pm 3$ kHz, (b) Herendeen and Silsbee's values of μ and Δ mentioned earlier, and (c) $T = 1.40$ °K. The dashed line represents the theoretical curve for $e^2Qq_0/h = 73.2$ kHz.

Our data show some trend towards a slightly large value of the quadrupole coupling constant $e^2Qq_0/h = 73$ kHz. This number is within the uncertainty of the original determination[1] of 71 ± 3 kHz, but in our opinion the spread in error in our data is too large and the limited number of measurements is too small to merit using it for a new determination of e^2Qq_0/h.

Resonance lines are observed to have a linewidth of 3 kHz between points of maximum slope at large (50 kV/cm) values of $\vec{E}_0$. The satellite lines narrow for values of $\vec{E}_0$ greater than about 30 kV/cm since the Stark effect overwhelms random strain broadening.

Figure 4 shows a plot of the splitting frequency versus the angle θ for an applied electric field of 48.3 kV/cm and an average temperature of 1.41 °K. The solid curve is the calculated curve $f_Q = 16.08 \cos 2(\theta - 1.8°)$ kHz. The 1.8° shift from $\theta = 0$ is not considered significant in view of the experimental uncertainties. The value of $\eta = 1$ for the average electric-field-gradient asymmetry parameter is established by the angular dependence of the data.

In summary, the electric-field-induced quadrupole splittings of Li^7 in KCl:Li^+ have been observed. The functional dependence of the splitting on the magnitude of the electric field exhibited the saturating character (Fig. 3) predicted by the theoretical $\langle 111 \rangle$ tunneling model of GBK and the averaging method previously employed.[1] In addition, the predicted sinusoidal dependence of f_Q upon θ is well borne out.

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†Work supported in part by the National Science Foundation, under Grant No. GP-9343, and the Advanced Research Projects Agency through the Cornell University Materials Science Center, Report No. 1494.

*Based in part upon the thesis submitted in partial fulfillment of the M. S. degree, Cornell University, 1970.

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