^{14}N and ^{39}K Nuclear Quadrupole Coupling in KNO_3 *

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The nuclear quadrupole interaction tensors of ^{14}N and ^{39}K in potassium nitrate at room temperature have been determined from nuclear magnetic resonance (NMR) rotation studies of single crystals at 9.4 T. Values for the coupling constants and asymmetry parameters at 296 K are

^{14}N: $e^2qQ/h = 751$ kHz, $\eta = 0.022$;
^{39}K: $e^2qQ/h = 1326$ kHz, $\eta = 0.171$.

The temperature dependence, on approaching the order-disorder phase transition near 401 K, is linear.

Introduction

In potassium nitrate, KNO_3, the ^{14}N nuclear quadrupole interaction is difficult to determine by powder methods because of its intermediate strength, which is too weak for direct determination by NQR and too strong for the first-order NMR powder singularities to be visible. The same is true of ^{39}K, though in that case the quadrupole interaction can be estimated from the $(1/2, -1/2)$ transition second-order line-shape. There is no strong NMR signal from an associated constituent nucleus which would permit a measurement for either ^{14}N or ^{39}K by double resonance methods. Accordingly, we have resorted to single-crystal rotation patterns of the quadrupole-perturbed NMR spectra to determine the quadrupole interactions.

Potassium nitrate at room temperature (α phase) has the aragonite structure which is orthorhombic, space group **Pmcn**, $Z = 4$ [1]. A feature of this assignment is that the crystallographic (b, c) plane containing the potassium and nitrogen atoms is a mirror plane, so that the a-axis of the crystal must be a principal axis of the electric field gradient tensor at both nuclei. That means that one rotation about the a-axis (held normal to the field) is sufficient to determine each tensor [2]. When heated to about 401 K, the α phase transforms to a disordered calcite structure (β phase). On subsequent cooling, it passes briefly through a ferroelectric (γ) phase before reverting to the α phase.

We have made a complete determination, with respect to crystal axes, of the quadrupole interaction tensor of ^{14}N and ^{39}K at room temperature and have investigated their variation as the crystal is warmed towards the phase transition.

Experiment

NMR spectra were observed in a magnetic field of 9.40 T, using a Bruker MSL 400 spectrometer. Direct spectra ^{14}N and ^{39}K were obtained by Fourier transformation of the free induction decay following the solid echo pulse sequence: $(\pi/2)_x - t - (\pi/2)_y - t -$ acq. The pulse widths used were 4 μs for ^{14}N and 3 μs for ^{39}K; the values of t were 40 μs for ^{14}N and 100 μs for ^{39}K. Relaxation of both nuclei was fast enough to allow a repetition rate of 2 Hz. The operating frequency was 28.908 MHz for ^{14}N and 18.670 MHz for ^{39}K.

A polycrystalline specimen was used to obtain the spectrum of the $(1/2, -1/2)$ transition of ^{39}K given in Figure 1.

Single crystals of potassium nitrate were grown from aqueous solution. A number of similar shape in the form of rectangular bevelled tablets, with typical dimensions $2.5 \times 6 \times 8$ mm^3, was selected. The crystallographic orientation relative to the external faces was determined from X-ray Laue photographs of one of them: the longer edges of the crystal defined the axes a and b. This was sufficient to orient the other crystals by eye.

The crystal specimen was mounted with one of its crystallographic axes parallel to the rotation axis

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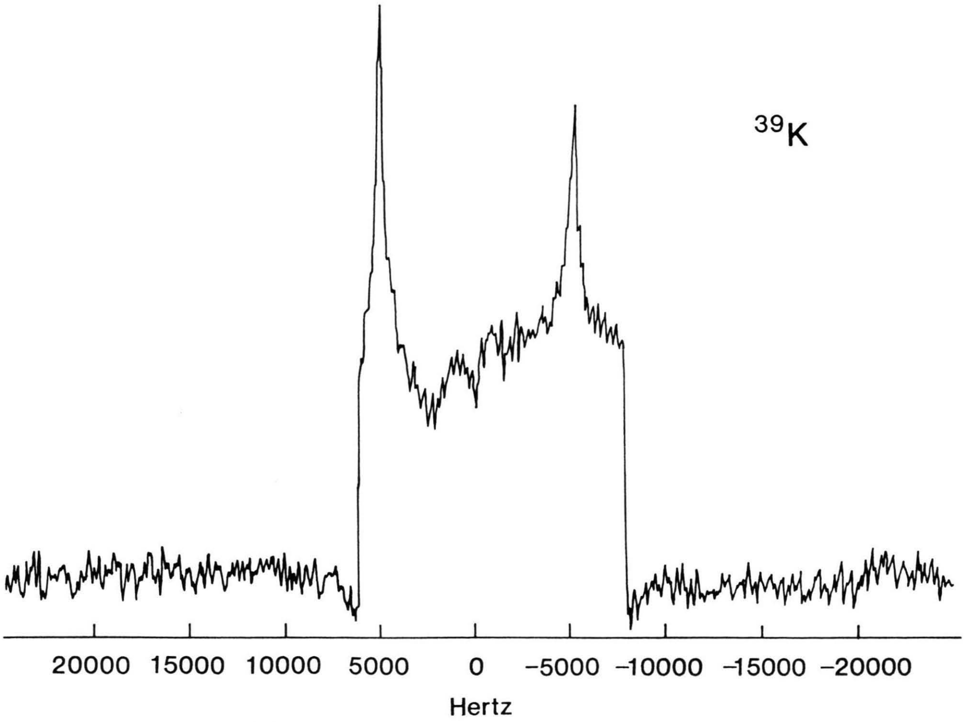

Fig. 1. NMR spectrum of ^{39}K in polycrystalline potassium nitrate at 296 K.

which, in turn, was perpendicular to the field. At angular intervals of 7.5°, spectra of the $\pm(I, I-1)$ transitions of ^{14}N ($I=1$) and ^{39}K ($I=3/2$) and the $(1/2, -1/2)$ transition of ^{39}K were recorded at 296 K. Typical linewidths (f.w.h.m.) were 200 Hz for ^{14}N, and 250 Hz and 50 Hz for the satellite and central transitions, respectively, of ^{39}K. Chemical shift tensors were later extracted from the ^{14}N spectra and from the central transition of ^{39}K (where the anisotropy is indeed small): those results will be reported elsewhere.

At selected angular settings on the *a*-axis rotation, the $\pm(I, I-1)$ transitions of ^{14}N and ^{39}K were observed while the specimen was heated from room temperature with a nitrogen flow system. For ^{14}N, the settings were $\sphericalangle(c, B)=0°$, 45° and 90°; for ^{39}K, $\sphericalangle(c, B)=22.5°$ and 112.5° were chosen, close to principal axes of one of the sites (explained below). The highest temperature at which resonances were seen was 399 K. On further heating, cracking and other irreversible processes occurred, presumably associated with volume expansion at the phase transition near 401 K, and no NMR signals were detected above that temperature. On subsequent cooling to 385 K and below, only broadened resonances characteristic of the α phase were observed.

Analysis

1. Powder Spectrum

Figure 1 shows the powder average of the ^{39}K second-order quadrupole-shifted $(1/2, -1/2)$ transition. Measurement of the singularities yields the estimates,

$$^{39}\mathrm{K}:\quad e^2 qQ/h = 1322\,\mathrm{kHz},\quad \eta = 0.173,$$

if chemical shielding anisotropy is ignored.

2. Rotation Patterns

The resonances have been paired by graphical assignment, and their frequency separations studied as functions of rotation angle. The resulting rotation patterns consist of simple sinusoids of period 180°, characteristic of first-order quadrupolar splitting.

Figures 2 and 3 show the *a*-axis rotation patterns. It is clear that this rotation shows splitting from two sites which differ only in their opposite orientation with respect to *b* (or *c*); the angular displacement (α) from the axes *b* and *c* is small for ^{14}N and about 22° for ^{39}K. During rotation about the *b* or *c*-axis (not reproduced here) the two ^{14}N splittings remain coincident (to within our ability to orient the crystal and the rotation axis relative to the field). This is consistent

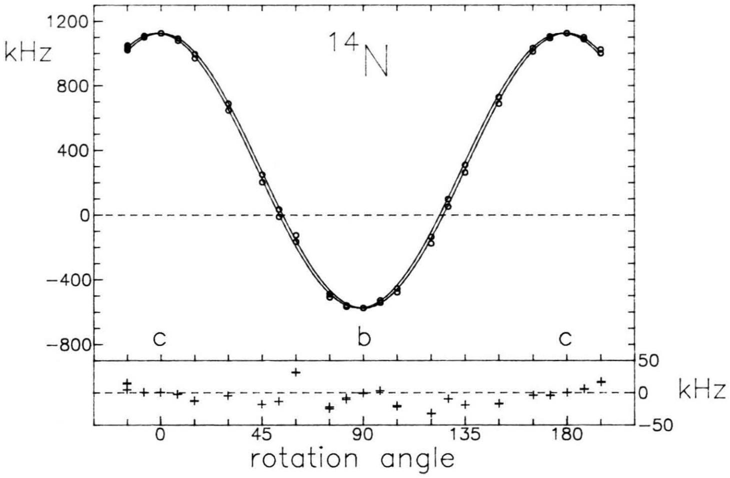

Fig. 2. Rotation pattern of ^{14}N NMR splitting in a single crystal of potassium nitrate at 296 K: rotation axis a is normal to field B, rotation angle $\omega = 0$ where $c \parallel B$. (○) Measured splittings; curves calculated using the parameters of Table 3 and offset angle of $-1.02°$; (+) residues, plotted on a 4-fold expanded scale.

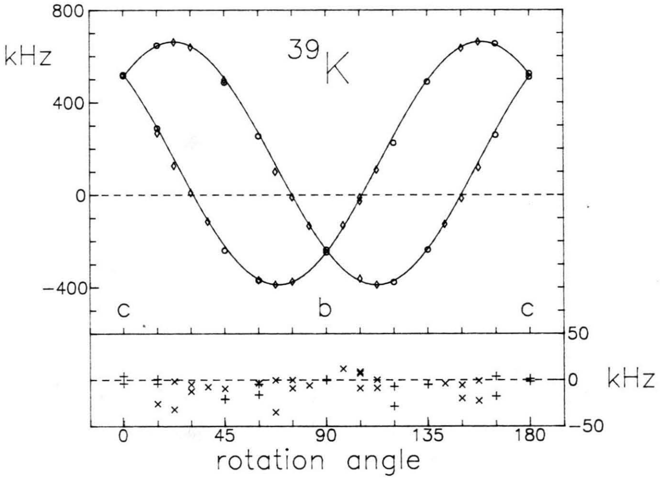

Fig. 3. Rotation pattern of half the separation of the ^{39}K NMR satellites in potassium nitrate at 296 K, using the same crystal and rotation as in Figure 2. (○) Measured values used for fitting; (◇) other measured values; curves calculated from the parameters of Table 3 and offset angle of 0.48°; residues of (+) fitted and (×) other measurements, plotted on a 4-fold expanded scale.

with the point group symmetry **mmm** of the structure with $Z = 4$, which has two magnetically inequivalent molecules. For both sites, one of the principal axes, located where the splitting is stationary, lies along the a-axis of the crystal. This is in accordance with the site symmetry **m** already mentioned.

Observed splittings have been fitted with sinusoidal functions by a method of extended least squares which we have used before [3]. The method achieves accuracy by effectively giving greater weight to measurements near the turning-points. Owing to short-sighted programming, only about half the measurements of ^{39}K could be included in the fitting procedure.

The frequency separation between the transitions $(m, m-1)$ and $(1-m, -m)$ can be described by the component in the laboratory frame ($Oxyz$, $Oz \parallel B$) of a symmetric tensor ν_Q which is fixed in the crystal [3]:

$$\nu_m - \nu_{1-m} = (2m-1)(\nu_Q)_{zz}.$$

Here $m = I$ for each nucleus. The tensor ν_Q is named for its primary eigenvalue, the quadrupole frequency (conventionally designated ν_Q), which is such that $e^2 qQ/h = (2/3)\,I\,(2I-1)\,\nu_Q$.

The quadrupole frequency tensor is transformed to a cartesian frame (with axes 1–3) in the crystal, coinciding with the respective crystal axes (a, b, c), in the manner of Volkoff [2, 3]. The angular origin of each rotation has been adjusted slightly to conform with the point group symmetry, corresponding to Volkoff's case (1) adjustment [2]. The results are given in Tables 1 and 2. The composite tensor of Table 1 is formed by weighting the rotations by their angular

Table 1. ^{14}N quadrupole frequency tensor (kHz), components with respect to crystal axes, 1, 2, 3; range of observation (°).

Rotation axis	*a*	*b*	*c*	Composite
Range	210	90	90	
11	−550.650 (19)	−550.9757 (7)	−549.9393 (7)	−550.56 (26)
22	−575.023 (15)	−574.6580 (11)	−574.9867 (7)	−574.93 (11)
33	1125.673 (15)	1125.6337 (7)	1124.9260 (10)	1125.49 (22)
12	...	...	0.0000 (5)	0.0000 (5)
31	...	0.0000 (6)	...	0.0000 (6)
23	±23.643 (16)	...	...	±23.643 (16)

Table 2. ^{39}K quadrupole frequency tensor (kHz), components with respect to crystal axes 1, 2, 3; range of observation (°).

Rotation axis	*a*
Range	180
11	−274.808 (59)
22	−242.485 (46)
33	517.293 (46)
12	...
31	...
23	±363.236 (39)

Table 3. Nuclear quadrupole interaction tensors in potassium nitrate at 296 K. Quadrupole coupling constant (kHz); asymmetry parameter; angles (°) between principal axes *X*, *Y*, *Z* and crystal axes *a*, *b*, *c*.

Nucleus	^{14}N	^{39}K
$\lvert e^2 q Q h^{-1} \rvert$	750.55 (15)	1326.01 (9)
η	0.0219 (2)	0.17102 (11)
$\sphericalangle$ (Z, c), (Y, b)	±0.7964 (6)	±21.858 (2)
$\sphericalangle$ (X, a)	0.0000 (12)	n.m.

range, and its errors are given by external consistency, due to misorientation of the rotation axis in the crystal. Table 2 with only one rotation is sufficient, but the fitting errors do not include errors due to such misorientation. The results of principal axis transformation are collected in Table 3. The principal values for ^{39}K agree with the powder estimates.

Quadrupole frequency components $(\nu_Q)_{zz}$ for an *a*-axis rotation, calculated from the parameters of Table 3 and the appropriate angular offset, are compared with the observed splittings in Figs. 2 and 3.

3. Temperature Variation

The tensor ν_Q can be studied as a function of temperature by making measurements at three different orientations of the field with respect to the crystal and assuming that the point group symmetry is invariant. Averaging the splittings from the two sites gives directly $(\nu_Q)_{33}$ at orientation ⟨001⟩ and $(\nu_Q)_{22}$ at ⟨010⟩, while their difference gives $(\nu_Q)_{23}$ at cartesian ⟨011⟩: all these quantities are stable to misorientation of the crystal. For ^{14}N, measurements at different angles have first been brought to a common temperature by graphical smoothing. The results of principal axis transformation are shown for ^{14}N in Figure 4.

The ^{39}K measurements were made, at the same temperatures, for two orientations 90° apart. In this case the quadrupole frequency tensor can be recovered with the aid of an adjustable angle; once again the point group symmetry is assumed [3]. Given the nominal setting ω, the direction cosines of the magnetic field are allowed to have been mis-set, $(3, z) = \cos(\omega + \varepsilon)$ in one orientation, $(3, z) = \sin(\omega - \varepsilon)$ in the other, $(1, z) = 0$ in both. At any temperature there are then four measured splittings (two sites, two orientations) to provide three unknown components (22, 23, 33) and one angle ε which consistency requires to be constant. In the case of ^{39}K we found that ε remained satisfactorily within the range $(0.7, 0.9)°$ over four temperatures. The mean value of ε produces the results shown in Figure 5. The temperature-independent error in coupling constant is of order 4 kHz, in asymmetry 0.005, in angle α 1°.

Discussion

1. Nuclear Quadrupole Coupling

The nuclear quadrupole interactions at room temperature are summarized in Table 3. Their temperature variation is small and linear, showing no premonitory deviation as the order-disorder phase transition is approached, unlike the case of $NaNO_3$ [4]. The decrease of the coupling constant with temperature is $3.7 \times 10^{-4}\ K^{-1}$ for ^{14}N and $9 \times 10^{-4}\ K^{-1}$ for ^{39}K.

The ^{14}N quadrupole coupling constant at room temperature, $e^2 q Q h^{-1} = 751$ kHz, is comparable with other nitrates, $NaNO_3$ (745 kHz [4]) and $Ba(NO_3)_2$ (651 kHz [5]). The asymmetry parameter, however, is nonzero in KNO_3, where the NO_3 group has less than trigonal symmetry. In a neutron diffraction study, Nimmo and Lucas located one of the NO_2 planes in the molecule parallel to the (a, b) plane of the crystal and the other O atom slightly displaced from it [1]. The small separation of the curves in Fig. 2, $\alpha = \pm 0.80°$, is the NMR evidence for the molecular tilt. In the other nitrates [4, 5], the primary principal axis *Z* is fixed by the trigonal symmetry. The orientation of the *Z* axis and the small temperature-dependence of the interaction parameters (Fig. 4) indicate that the

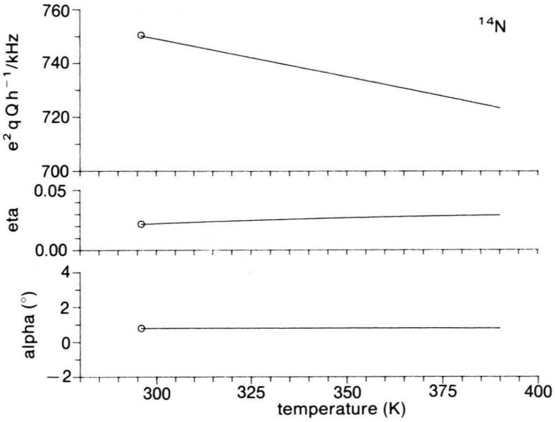

Fig. 4. Temperature dependence of ^{14}N quadrupole interaction tensor in KNO_3, α phase. Coupling constant; asymmetry parameter; orientation $\alpha = \sphericalangle (Z, c)$. Curves derived from measurements at three crystal settings, smoothed over several temperatures; (o) values obtained from rotation study.

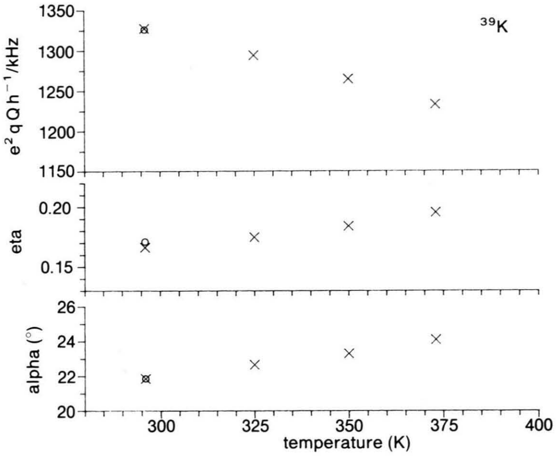

Fig. 5. Temperature dependence of ^{39}K quadrupole interaction tensor in KNO_3, α phase. Coupling constant; asymmetry parameter; orientation $\alpha = \sphericalangle (Z, c)$. (×) Values inferred from measurements at two crystal settings; (o) values obtained from *a*-axis rotation.

nuclear electric field gradient is mainly intramolecular in origin, as expected [4].

The ^{39}K quadrupole coupling constant at room temperature, $e^2qQh^{-1} = 1326$ kHz, is comparable with that found in $KClO_3$ (995 kHz [6, 7]), $KBrO_3$ (968 kHz [8]), KOH (1682 kHz [9]) and KH_2PO_4 (1680 kHz [10]); it falls in the narrow range which has been noted for a number of other potassium salts [11]. It is similar to the coupling constant in $KReO_4$ (1148 kHz [12]) but not KIO_4 (102 kHz [13]) at room temperature.

2. *Crystal Field Calculation*

Structural studies have shown that in the α phase the NO_3 group has less than maximum symmetry. According to the refinement of Nimmo and Lucas [1], the mean position of the three O atoms is displaced from the N position by 0.0105 (13) Å at 298 K. Such a polar distortion is likely to be related to the crystal field acting on the molecular ion and would also affect the ^{14}N quadrupole coupling. The field may be modelled by point charges (q) on each atom, with $q\,(\mathrm{K}) = e$ and $q\,(\mathrm{O1}) = q\,(\mathrm{O2}) = -[e + q\,(\mathrm{N})]/3$. Taking the positional parameters at 298 K from [1] and using our lattice-sum program EFG5, we have computed the field at the N site due to the charges outside the home molecule.

If the charge parameter $q\,(\mathrm{O})/e$ is chosen in the range $(-0.45, -1.44)$, which is compatible with other studies of the nitrate group [14], then the resulting local field has the same direction as the molecular dipole from O_3 to N (with its experimental uncertainty), and its strength falls in the range (0.13, 0.19) V Å^{-1}, respectively.

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