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The Temperature Dependence of the Quadrupole Coupling Constant of ^{23}Na in Sodium Nitrate

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Sodium nitrate (Na NO_3) shows an unusually rapid decrease of the ^{23}Na quadrupole coupling constant with temperature, as reported by Eades et al (1958). New measurements have been made with two other single crystals and have been extended to liquid air temperature. The results are shown in figure 1. As pointed out by Eades et al this behaviour cannot be explained by thermal lattice expansion nor cooperative re-orientation or disordering of the nitrate groups.

The purpose of this paper is to show that the decrease of the quadrupole coupling constant may be accounted for by a motion of the sodium nucleus itself. This will be proved by showing that there are in the vicinity of the sodium site certain regions where the electric field gradient caused by surrounding ions is much smaller or even of opposite sign.

In the Na NO_3 crystal all ^{23}Na nuclei are situated in equivalent positions and on the trigonal axis. The field gradient at a ^{23}Na nucleus arising from a neighbouring ion of charge $\varepsilon_j e$ may be expressed as

$$\mathrm{eq} = \varepsilon_j e\,(3\cos^2\theta_j - 1)/r_j^3$$

where r_j and θ_j are the spherical polar coordinates of the neighbour in a system centred on that nucleus and with its Z axis parallel to the trigonal axis. The value of the field gradient at the site of the sodium nucleus can be obtained by summing this expression over all neighbours. Unfortunately this summation converges very slowly and must therefore be taken over an extremely large number of neighbours. Bernheim and Gutowsky (1960) who had available an electronic computer have shown that the summation must be taken to 50 Å if an accurate answer is required. Their calculations which were for the sodium ion in its equilibrium posi-

tion only gave a result of eq $= +19.54 \times 10^{-3}$ e Å^{-3}, and this is in agreement with the previous calculation made by Bersohn (1958).

By computing only the difference between the field gradients at two adjacent points these tedious calculations have been avoided. This difference converges much more quickly so that summation over the few nearest neighbours gives sufficient accuracy for qualitative considerations.

The quick convergence of the field gradient difference between points on the trigonal axis can be easily explained. In the vicinity of the equilibrium position of the sodium ion the field gradient can be expressed as a series, namely:

$$\text{eq}\,(z) = \text{eq}\,(0) + e\frac{dq}{dz}z + \frac{e}{2}\frac{d^2q}{dz^2}z^2 + \ldots..$$

where z is the distance from the equilibrium position. From the structure of the lattice it follows that $q(z) = q(-z)$ and therefore all odd derivatives vanish. This means that the difference $d = e[q(z) - q(o)]$ depends on terms inversely proportional to r^5 and higher.

A calculation of d, for $z = 0.503$ Å (i.e. 3% the cell diagonal), gave the result $+ 25.4 \times 10^{-3}$ e Å^{-3}. Although the summation only included neighbours up to 7.6 Å, 81% of the result came from the nearest 6 oxygen and nearest 6 sodium ions (at the distance at 2.407 Å and 4.044 Å respectively; a value of $\varepsilon = -\frac{1}{3}$ was assumed for every oxygen atom). When combined with the known $eq(o)$ it is clear that the displacement of the sodium ion along the trigonal axis results in an increase of the quadrupolar coupling constant.

A somewhat different approach has been chosen to investigate the effect of the sodium ion in the plane perpendicular to the trigonal axis. It is assumed (as an example) that the nucleus is moving within a circle of radius R on this plane and that the probability of finding it is constant over this circle. The field gradient at any point inside the circle $r = \delta$ ($\delta \leqslant$ R), $\theta = \frac{\pi}{2}$ and $\text{Ø} = \text{Ø}$ caused by a neighbouring ion j is

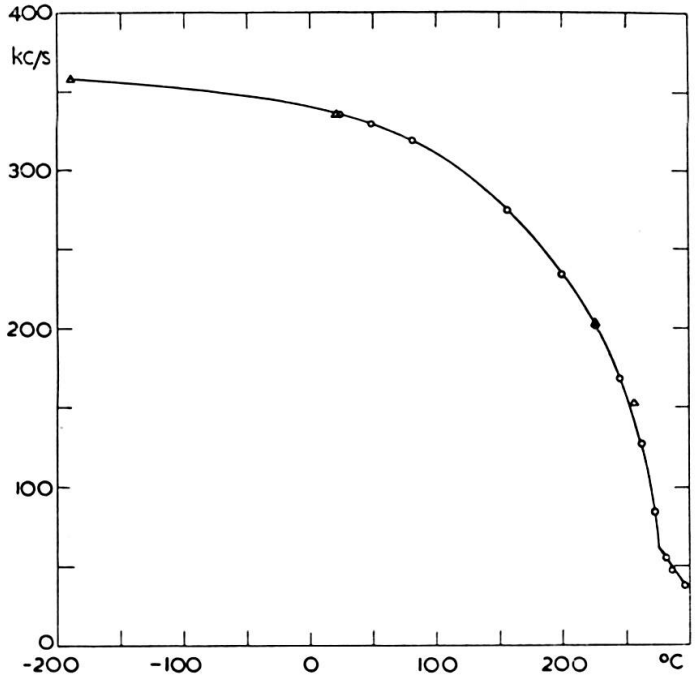
$$\frac{r_j^2(3\cos^2\theta_j - 1) - \delta^2 + 2r_j\delta\sin\theta_j\cos\text{Ø}}{r_j^5\left(1 + \frac{\delta^2}{r_j^2} - 2\frac{\delta}{r_j}\sin\theta_j\cos\text{Ø}\right)^{\frac{5}{2}}}z_j e$$

This expression may be converted into a form more suitable for averaging by expanding the denominator as the series $(1 - x)^{-n}$ where $x < 1$. Terms

higher than δ^2/r^2 are neglected and the expression is averaged over a circle of radius R. This gives the result

$$z_j e\,\overline{[q(0) - q(\delta, \varnothing)]} = \frac{5}{4} R^2 r^{-5}\left[(3\cos^2\theta - 1)\left(\frac{7}{2}\sin^2\theta - 1\right) + 2\sin^2\theta - \frac{2}{5}\right] z_j e$$

Again this difference depends on r^{-5} and consequently the summation need only be taken to 5.1 Å. If R is assumed to be 0.503 Å which satisfies



The variation with temperature of the electric quadrupole coupling constant $e^2\,Qq/h$ (expressed in kc/s) of the ^{23}Na nuclei in a single crystal of sodium nitrate. eQ is the nuclear electric quadrupole moment, eq is the electric field gradient along the crystal axis, and h is Planck's constant. Obtained by nuclear magnetic resonance method in a magnetic field of 4,5 k oersted.

the condition $\frac{\delta^2}{r^2} \ll 1$, the field gradient difference obtained by summing over neighbours to 5.1 Å is -6.04×10^{-3} e Å^{-3}. This shows that a small oscillation of the sodium nuclei in the plane perpendicular to the trigonal axis can cause a considerable decrease in the quadrupole coupling constant. This effect is almost entirely due to the six nearest oxygen atoms.

Although in these calculations the sodium ions have been assumed to move in a fixed array of surrounding ions, it is their relative motion

which is significant, and the same result would follow if the nitrate groups moved in the same manner relative to fixed sodium ions.

The effect of spatial oscillations of the sodium ions have also been considered. Assuming a spherically symmetric probability distribution a similar consideration leads to the result that the mean field gradient difference is zero.

Conclusion.

The rapid decrease of the ^{23}Na quadrupolar coupling constant in $Na\,NO_3$ with temperature may be explained by assuming that the sodium ion moves predominantly in the plane perpendicular to the trigonal crystal axis. This decrease is largely due to the electric field gradient caused by the six nearest oxygen atoms.

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DISCUSSION

M. Kastler. — In $NO_3\,Na$ crystals there is a second order phase transition below the melting point.

How does this appear in the temperature variation of the quadrupole splitting ?

M. Hennel. — The phase transition shows up as a change in the slope of the quadrupole coupling constant versus temperature curve as seen in fig. 1. If, as has been suggested, the phase transition marks the onset of rotation of the nitrate groups then it can be shown that this has only a small effect on the quadrupole coupling constant.