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## OF THE $NaXO_2$ TYPE (X = In,Cr,Ti,Tl,Al,Sc)

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## ABSTRACT

The $^{23}Na$ nuclear quadrupole coupling constant is calculated for six compounds of the $\alpha$-$NaFeO_2$ type, namely $NaInO_2$, $NaCrO_2$, $NaTiO_2$, $NaTlO_2$, $NaScO_2$, and $NaAlO_2$. We assume point charge distribution at the lattice sites and take into account the effect of charges and effective (induced) oxygen dipole moments within a sphere of 50 Å around the site of interest. These calculations emphasize the importance of the dipolar contributions with resultant polarizabilities in the range $(0.2 - 1.4 \text{ Å}^3)$ in agreement with the results previously obtained by calculations of the EFG at the Fe site in $\alpha$-$NaFeO_2$, $CuFeO_2$ and $AgFeO_2$.

## INTRODUCTION

Some authors (Bersohn 1958, Bernheim and Gutowsky 1960, Belford et al 1961, Taft et al 1974 and 1975) have discussed the electric field gradients and nuclear quadrupole constants in "ideal ionic crystals". The electric field gradient in such a lattice arises from charges external to the ion. Complex oxides and sulfides of the $AMX_2$ type such as $\alpha$-$NaFeO_2$, $NaInO_2$ and $NaInS_2$ are expected to be reasonable approximations to such crystals (Peterson and

Bridenbaugh 1969, Taft et al 1974 and 1975).

Peterson and Bridenbaugh (1969) did a particularly interesting job of calculating the quadrupole coupling constants for compounds of the $\alpha$-NaFeO$_2$ type and varied the charge distribution of the constituent atoms in order to obtain a fit with the experimental values. He suggested however that the polarizability of the oxygen ions should be considered in order to improve these calculations. It was noticeable that the charges on the trivalent metals obtained for various compounds were most unlikely. There was also some inconsistency in the sign of the field gradient resulting from these calculations.

Recently EFG calculations (Taft 1975) at the Fe site in $\alpha$-NaFeO$_2$, CuFeO$_2$ and AgFeO$_2$ were used to fit the Mössbauer experimental results. These calculations indicated that the oxygen dipolar contributions were dominant and necessary to obtain a good fit with the experimental values.

Encouraged by these results we decided to extend these calculations to the $\alpha$-NaFeO$_2$ type compounds previously studied by Peterson and Bridenbaugh (1969), i.e., NaMO$_2$ (M = In, Cr, Ti, Tl, Al, Sc).

It is interesting to note that the dipolar contributions also appears to be important in these compounds and parameters such as the sign of the field gradient and oxygen dipole polarizabilities are consistent with the type of results obtained for $\alpha$-NaFeO$_2$, CuFeO$_2$ and AgFeO$_2$.

CALCULATIONS OF THE FIELD GRADIENT

Compounds of the $\alpha$-NaFeO$_2$ type have space group R$\bar{3}$m. For hexagonal

axes and cells the atoms are in position

$$(0,0,0; \quad \frac{1}{3}, \frac{2}{3}, \frac{2}{3} ; \frac{2}{3}, \frac{1}{3}, \frac{1}{3}) +$$

Na: (3a)  0, 0, 0

M : (3b)  $0, 0, \frac{1}{2}$

O : (6e)  $0, 0, Z ; 0, 0, \overline{Z}$

The site symmetry of the various atoms are as follows:

Na:  $\overline{3}m$ ,

M :  $\overline{3}m$ ,

O :  $3m$

In Table 1 are summarized the crystallographic data for the six compounds considered in this paper. It is to be noted that the M atom is at the origin, thus the Z parameter may be somewhat different than that given in the references (Peterson and Bridenbaugh 1969).

We determine the effective dipoles at the respective lattice sites from the equation :

$$\mu_{eff} = \alpha F_{(\mu_{eff}, charges)} \qquad (1)$$

$\alpha$ is the polarizability of the ion and $F_{(\mu_{eff}, charges)}$ is the electric field arising from the effective dipole moments and neighboring charges. The components of the electric field at a point $(x,y,z)$ due to an ideal point charge $e$ at $(0,0,0)$ can be evaluated from the equations :

$$F_x = \frac{ex}{r^3} \qquad F_y = \frac{ey}{r^3} \qquad F_z = \frac{ez}{r^3} \qquad (2)$$

The effect of an ideal point dipole $(m_x, m_y, m_z)$ is given as :

$$F_x = \frac{3x^2-r^2}{r^5} \, m_x + \frac{3\,x\,y}{r^5} \, m_y + \frac{3\,x\,z}{r^5} \, m_z \tag{3}$$

$$F_y = \frac{3\,x\,y}{r^5} \, m_x + \frac{3y^2-r^2}{r^5} \, m_y + \frac{3\,y\,z}{r^5} \, m_z \tag{4}$$

$$F_z = \frac{3\,x\,z}{r^5} \, m_x + \frac{3\,y\,z}{r^5} \, m_y + \frac{3z^2-r^2}{r^5} \, m_z \tag{5}$$

where $r = (x^2 + y^2 + z^2)^{1/2}$.

The electric field at the Na and M sites is zero because of the symme-
try and hence $(\mu_{eff})_{Na} = 0$, $(\mu_{eff})_M = 0$. The oxygen ions in the unit cell are
equivalent, the magnitude of the field at both sites is the same but not the
orientation which can be determined by our calculations.

In order to obtain the dipole moments on the $O^{--}$ ions, it is necessary
to calculate the electric field at the $O^{--}$ sites. Since the dipoles themselves
contribute to the electric field, this must be calculated self-consistent (Raj
and Amirthalingham 1966). We have thus calculated the effective dipole-moments
and the effective field F from the method of iteration. To begin with, we assu-
me that the electric field $(F_{01}, F_{02})$ at the oxygen sites originate from charges
only within a selected sphere. The dipole moments at the oxygen sites will be
given by $\alpha \; F_{01}$ and $\alpha \; F_{02}$, where $\alpha$ denotes the oxygen polarizability. These
dipoles also contribute to the field and let us denote the contributions as
$F_{d1}^1$ and $F_{d2}^1$ at both oxygen sites. The total dipoles at these sites will be
equal to $\alpha \; (F_{01} + F_{d1}^1)$ and $\alpha \; (F_{02} + F_{d2}^1)$. The superscript denotes the number
of cycles. The values are changed to $\alpha \; (F_{01} + F_{d1}^2)$ and $\alpha \; (F_{02} + F_{d2}^2)$ in the
next cycle and so on. These cycles are repetead until the values obtained are
the same as in the preceding cycle. Self consistent values are obtained in 20

to 30 cycles.

Then, we have a lattice with sites characterized by their respective effective charges and effective dipole moments, both of which contribute to the electric field gradient tensor.

The general formulas for the fields gradients are given by: Effect of Charges

$$q_{xx} = (\frac{e}{r^3})(\frac{3x^2}{r^2} - 1) \qquad q_{yy} = (\frac{e}{r^3})(\frac{3y^2}{r^2} - 1) \qquad q_{zz} = (\frac{e}{r^3})(\frac{3z^2}{r^2} - 1)$$

$$q_{xy} = \frac{3e\ x\ y}{r^5} \qquad q_{yz} = \frac{3e\ y\ z}{r^5} \qquad q_{zx} = \frac{3e\ z\ x}{r^5}$$

(6)

Effect of Dipoles

$$q_{xx} = \frac{-3(r^2-5x^2)(xm_x + ym_y + zm_z)}{r^7} - \frac{6\ xm_x}{r^5}$$

$$q_{yy} = \frac{-3(r^2-5y^2)(xm_x + ym_y + zm_z)}{r^7} - \frac{6ym_y}{r^5}$$

$$q_{zz} = \frac{-3(r^2-5z^2)(xm_x + ym_y + zm_z)}{r^7} - \frac{6zm_z}{r^5}$$

(7)

$$q_{xy} = \frac{-3(xm_x + ym_y)}{r^5} + \frac{15yx(xm_x + ym_y + zm_z)}{r^7}$$

$$q_{yz} = \frac{-3(ym_z + zm_y)}{r^5} + \frac{15yz(xm_x + ym_y + zm_z)}{r^7}$$

$$q_{zx} = \frac{-3(zm_x + xm_z)}{r^5} + \frac{15xz(xm_x + ym_y + zm_z)}{r^7}$$

In the actual calculation, the effects at the point $(x,y,z)$ of charges and dipoles at respective points $(x_i,y_i,z_i)$ are obtained by suitable transfor-

ming the eqs. (2) to (5) i.e., by substituing $x - x_i$ for $x$, $y-y_i$ for $y$ etc.

The nine components of the EFG tensor are calculated in an arbitrary orthogonal coordinate system, using a selected range of dipole polarizabilities. The lattice sum calculations of these components were carried out on a high speed IBM 370 computer by considering the effect of all sites within a chosen radial distance from the Na ion and this radius of summation was systematically varied untill the convergence was attained. All final results are calculated within a sphere of 50 $\overset{o}{A}$ radius. The trace of the corresponding symmetric matrix is zero. The matrix is diagonalized and q is the maximum eigenvalue obtained. The nuclear quadrupole coupling constant $(e^2qQ(1-\gamma_\infty))$ was calculated by using 5.197 for the shielding factor $(1 - \gamma_\infty)$ and +0.087 for the quadrupole moment of sodium (Peterson and Bridenbaugh 1969).

2 ## RESULTS AND DISCUSSION

The choice of dipole polarizability $\alpha$ for $0^{-2}$ to be used in equation (1) is a rather involved question. Some authors (Taylor and Das 1964, Sharma and Das 1964, Artman 1966, Rao and Rao 1967, Hudson and Whitfield 1967, Evans et al 1971, Kirsch et al 1974) have used values within the range $(0.2-1.4 \overset{o}{A}{}^3)$. Calculations (Taft 1975) in $\alpha$-NaFeO$_2$, CuFeO$_2$ and AgFeO$_2$ yielded polarizability values of 0.8-1.4 $\overset{o}{A}{}^3$. The smaller cell volumes for some of the compounds considered in this paper suggest polarizability values for this work on the order of $(0.3-1.4 \overset{o}{A}{}^3)$.

In regards to covalency in these crystals (NaXO$_2$) the relativity large X-O electronegativity difference and the octahedral coordination of X argues against the possibility of much covalent bonding (Taft 1974). It has also been noted by Kirsch et al (1974) that covalency effects were not important in their EFG calculations.

We have thus assigned a trivalent charge to the metal ions and have investigated the theoretical variation of the $^{23}Na$ nuclear quadrupole coupling constant as a function of the oxygen dipole polarizability.

Our calculations indicate that substantial dipole moments which cannot be neglected are induced at the oxygen sites in these compounds, leading to major contributions to the field gradient.

In Table II we have listed the polarizability values required to fit the experimental values (table III) of quadrupole coupling constant obtained by (Peterson and Bridenbaugh 1969). As opposed to this work we obtain consistent negative values for the sign of the field gradient in all six compounds.

As may be noted (Table II) the resultant polarizability values $(0.2-1.4 \, A^3)$ are in the expected range. The variation of dipole polarizability of oxygen ion in this set of compound of around $1 \, A^3$ is in agreement with others authors (Tessman and Kahn 1953, Brum and Hafner 1962, Evans and Hafner 1971, Kirsch et al 1974).

It has been suggested that the polarizability values should increase with the available volume for oxygen ion (Tessman and Kahn 1953, Kirsch et al 1974). As expected (Table II) the larger polarizabilities correspond to the compounds with larger values of cell volumes ($\Delta V$).

The polarizability $(1.34-1.43 \, A^3)$ as well as cell volume ($\Delta V$) values $(142-161 \, A^3)$ obtained for oxygen in $NaTiO_2$, $NaInO_2$ and $NaScO_2$ are in good agreement with the polarizability $(1.0-1.4 \, A^3)$ and $\Delta V$ values $(126-148 \, A^3)$ previously obtained in $AgFeO_2$, $\alpha$-$NaFeO_2$ and $CuFeO_2$ (Taft 1975). The polarizabilities and cell volumes in $NaTiO_2$, $NaCrO_2$ and $NaAlO_2$ are quite small.

There thus appears to be two narrow extreme ranges of polarizabilities in this set of compounds.

Kirsch et al (1974) obtained a variation of the dipole polarizabilities of the oxygen ion between 0..5 and 1.5 $\overset{o}{A}{}^{3}$. This is in agreement with our work. However, we do not obtain as they do a continuous evolution of polarizabilities values will the space occupied by the oxygen ion ($r_o$) defined as the distance X-0 minus the Goldsmith radius of X. The compounds studied in this paper have a larger range of $r_o$ values than those considered by Kirsch et al (1974). Our resultant polarizabilities ($\alpha$) appear to be the limiting values of the expected range of $\alpha$ values.

We would like to note, that the higher multiple moments (electric quadrupoles) could also alter the results of these calculations. However, Kirsch et al (1974) concluded from their calculations that these effects were not important.

Summarizing, the present calculations substantiate the independent results obtained for $CuFeO_2$, $AgFeO_2$ and $\alpha$-$NaFeO_2$ emphasizing the importance of the oxygen dipolar contributions to the EFG tensor in compounds of the $\alpha$-$NaFeO_2$ type.

These calculation also suggest that nuclear resonance experiments may serve as usefull tools for obtaining information regarding polarizability values in crystalline complexes.

TABLE I

CRYSTALLOGRAPHIC DATA

| Compounds | $a_0 (\overset{o}{A})$ | $c_0 (\overset{o}{A})$ | Z Oxygen for M metal at origin |
|---|---|---|---|
| $NaInO_2$ | 3.235 | 16.35 | .257 |
| $NaCrO_2$ | 2.96 | 15.90 | .280 |
| $NaTiO_2$ | 3.02 | 16.20 | .280 |
| $NaTlO_2$ | 3.353 | 16.51 | .257 |
| $NaScO_2$ | 3.166 | 16.27 | .262 |
| $NaAlO_2$ | 2.868 | 15.88 | .272 |

TABLE II

CALCULATION OF POLARIZABILITIES IN $NaMO_2$
COMPOUNDS CHARGE ON M METAL (+3.0)

| Compounds | Polarizability $(\overset{o}{A}^3)$ EFG Negative | Cell volumes $(\overset{o}{A}^3)$ |
|---|---|---|
| $NaTlO_2$ | 1.43 | 161.49 |
| $NaInO_2$ | 1.41 | 148.18 |
| $NaScO_2$ | 1.34 | 141.88 |
| $NaTiO_2$ | 0.23 | 128.54 |
| $NaCrO_2$ | 0.21 | 121.20 |
| $NaAlO_2$ | 0.20 | 113.64 |

## TABLE III

### EXPERIMENTAL VALUES OF NUCLEAR
### QUADRUPOLE COUPLING CONSTANTS

| Compounds | $e^2qQ(KHZ)$ |
|-----------|--------------|
| $NaInO_2$ | 1925 |
| $NaCrO_2$ | 3295 |
| $NaTiO_2$ | 3201 |
| $NaTlO_2$ | 538 |
| $NaAlO_2$ | 2362 |
| $NaScO_2$ | 3045 |

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