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ABSTRACT

The origin of the quadrupole splitting observed in the Mössbauer spectra of α-$NaFeO_2$ has been investigated using point charge model. The magnitude of the electric field gradient (EFG) is very sensitive to the values of u, the distorsion parameter of the anion sub-lattice. These calculations combined with the experimental results are used to deduce information about the relative ammount of distorsion in this compound. The sign of the EFG is positive.

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I. INTRODUCTION

Many[1-10] lattice sum calculations, using point-multipole moments models, have been carried out to determine the electric field gradient in crystals, which in turn are used to interpret the Mössbauer and Nuclear Quadrupole resonance data. The accuracy and reliability of such calculations depend on the precision of the atomic coordinates, proper assignment of effective charges at the lattice sites and the values of the multipole polarizabilities, the Sternheimer factors and nuclear quadrupole moment involved.

In the absence of one or more of these quantities, attempts have been made[5, 10, 11] to evaluate the physically acceptable values by making the quantitites in question as variable parameters to yield best fit EFG results.

Such a procedure may also be useful to improve the precision of these quantities determined by other techniques[5]. Particularly, the high sensitivity[4,6,12] of the lattice sum calculations on the precision of the values of atomic coordinates, may be used[2,4] to improve the X-Ray crystal structure results.

In this paper we use point charge model (P.C.M.) calculations with due consideration of covalency effects to deduce information about the distorsion parameter u, previously determined by X-Ray crystal structure analysis[13-15] for α-$NaFeO_2$

II. CALCULATIONS

In the absence of any magnetic ordering, the total quadrupole splitting in an iron compound is given by:

$$\Delta E_Q = 1/2 \; e^2 \; q \; Q \; (1 + \eta^2/3)^{1/2} \; (1 - \gamma_\infty)$$

where $q = V_{zz}/e$, e being the electron charge and V_{zz} is the second derivative of the potential V in the principal axis system. Q is the quadrupole moment of ^{57m}Fe 14.4 KeV state and η is the asymmetry parameter defined as

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$$

The values of V_{xx}, V_{yy} and V_{zz} are chosen in such a way that

$$|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$$

This limits the η values to be positive and to vary from 0 to 1. In general q and η have contributions both from valence electrons and lattice charges, but in the case of half or completely filled shells, the main contribution comes from the lattice, the valence contribution comes indirectly through Sternheimer antishielding factors. The iron in α-$NaFeO_2$ is in the Fe^{3+} (high spin) 3d $^6S_{5/2}$ state and thus a point charge lattice sum calculation of the field gradient is a valid approximation.

In order to determine q and η , the nine components of the EFG tensor V'_{ij}'s are calculated from the relation:

$$V'_{ij} = \sum_k Z_k \, (3 \, r_{ik} \, r_{jk} - \delta_{ij} \, r_k^2) \, / \, r_k^5$$
$$(i,j = x,y,z)$$

in an arbitrary orthogonal coordinate system. The tensor is then diagonalized to generate principal axis components, V_{zz} and η . The EFG is a traceless symmetric tensor and thus in practice one needs to calculate only

five independent components.

The index k in Eq. (3) denotes the number of lattice points covered in the summation and Z_k is the effective charge on the kth ion.

The lattice sum calculations were carried out on a high speed IBM 360 computer within a chosen radial distance from the central iron ion and this radius of summation was systematically varied until the convergence was attained.

The values of V'_{ij}'s for 40, 50 and 60 Å radii are given in Table I. As can be seen, the variation of individual values is less than 0.1%. All final results are calculated within a sphere of 60 Å radius. The X-Ray structure and all other relevant data used in these calculations is summarized in Table II.

Using these values of q and η and the latest[16,17] values of Q and $(1 - \gamma_\infty)$ as 1.87 barns and -10.4 respectively, the value of ΔE_Q was calculated.

The effects of covalency were investigated by placing a wide range of effective charges at the iron lattice sites. We assign charge + 1.0 to Na and the corresponding charge on sulphur was determined by the charge neutrality condition.

These calculations were repeated taking simultaneously into consideration variation of effective charges and oxygen distorsion parameter (u).

III. RESULTS AND DISCUSSION

In our previous work[11,18] we have shown that point charge model calculations can account for the observed quadrupole doublet separation once the effects of covalency are incorporated by placing effective charges at the lattice

sites. However in the case of α-$NaFeO_2$, the octahedral coordination of Fe, comparison of the sum of ionic radii of Fe^{3+} and O^{--} with the observed bond length, and the relativiely large Fe - O electronegativity difference (E.D.) argues against the possibility of much covalent bonding. This is also substantiated by the work of Peterson and Bridenbaugh[19] in which P.C.M. calculations constrained by NMR nuclear quadrupole coupling constants were used to determine the effective charges on the metals in a series of compounds with α-$NaFeO_2$ type structure.

They derived a linear relationship connecting the effective charges on the metals with the E.D. of the metal-ligand neighbor bonds and it was noted that for E.D. about or greater than 2.0 the bonds are essentially ionic.

In our case (α-$NaFeO_2$) the E.D. is 1.60 which yields from their linear plot an effective charge of about 2.8 i.e 90% ionic character.

Variation of effective charges on iron over a wide range in our P.C.M. calculations did not account for the observed quadrupole doublet separation[20,21] which suggests that in addition to covalency, one should also consider other factors such as X-Ray structure parameters.

Many refinements for X-Ray structure parameters for oxides are reported in the literature[6,22]. There are three available[13-15] X-Ray structure analysis for α-$NaFeO_2$ and the latest refinement[15] only reports slight changes in the lattice parameter values of a_h and C_h which changes our ΔE_Q very slightly.

Only very small changes in a_h and C_h are expected since these values are unequivocally defined by the periodicity of the lattice and thus very little scope is left for further refinement, whereas, the very meaning of u is

contingent upon an adequate definiton of the ionic centroid[4].

We then have calculated the EFG as a function of u, the distorsion parameter (Fig. 1) for various charge distributions.

We obtain a best fit with the observed field gradient[20,21] for values of u between 0.2275 and 0.2285. The vale for u available presently from X-Ray structure analysis is 0.222.

Muir et al.[12] have calculated point charge contribution to the EFG in $CuFeO_2$ (dellafossite) and have shown that a variation of the value of u parameter of oxygen from 0.111 to 0.108 yields good agreement between the calculated ΔE_Q value and the experimental results obtained from Mössbauer spectroscopy. It is interesting that recent refinement[22] of the X-Ray structure of this compound gives this value of u as 0.1066 (5).

Calculations for higher moments are in progress. However, in certain cases[4,8] the dipole and quadrupole contribution to the EFG are of opposite signs and thus may not contribute very significantly to the EFG.

Point charge model calculations were also performed by Hudson and Whitfield[5] to determine the u parameter for $CdFe_2O_4$ and $ZnFe_2O_4$.

They found a better agreement when they did not include the dipole contribution to the EFG.

The crystal structure of α-$NaFeO_2$ (low temperature phase of sodium orthoferrite) is a rhombohedral layer structure with space group D^5_{3d} - R $\bar{3}$m . Every iron atom occupies a crystallographically equivalent site, octahedrally surrounded by six oxygens. This site symmetry of iron atom ($\bar{3}$m) indicates an axially symmetric EFG and this is in agreement with our calculations.

This zero value of η also allows us to ascertain the sign of the EFG as positive. This sign remains unaltered throughout our variation of u(Fig. 1).

Our calculations also indicate that at $u \cong 0.2215$ the geometric factors of Fe and O lattice sites cancell and thus at this point the ΔE_Q values do not depend on the charge variation.

Summarizing our discussion we conclude that our point charge model calculations in conformity with Mössbauer quadrupole resonance data suggest the desirability of further refinement of X-Ray data in α-$NaFeO_2$

TABLE I - Values (in A^{-3} units) of the EFG tensor components for different spheres of radius R in an arbitrary orthogonal axes system.($u = 0.222$)

V'_{ij} \ R	40 A	50 A	60 A
V_{xx}	-0.171930890	-0.171987490	-0.171839906
V_{yy}	-0.146855905	-0.146904250	-0.146778191
V_{zz}	0.318786796	0.318891740	0.318618096
V_{xy}	0.241558664	0.241638185	0.024143083
V_{yz}	0.141743087	0.141789749	0.141668078
V_{zx}	0.086129603	0.086157956	0.086084024

TABLE II - X-Ray crystal structure and other relevant data used in this work

A. Cristal structure

Space Group $D^5_{3d} - R\bar{3}m$

with site symmetry of Na $\bar{3}$ m

Fe $\bar{3}$ m (Ref. 14, 15)

O 3 m

The unit cell parameters in rhombohedral description

$a_r = 5.59$ Å

$\alpha = 31^0\ 20'$

The unit cell contains 1 molecule with atomic positions as

Na at (1a) 0 0 0

Fe at (1b) 1/2 1/2 1/2

O at (2c) (u, u, u) with u = 0.222

In hexagonal description the lattice parameters are

$a_h = 3.036$ A

$C_h = 15.961$ A (Ref. 14)

Refined parameters

$A_h = 3.019$ A

$C_h = 15.934$ A (Ref. 15)

B. Ionic Radii

$Na^+ = 0.95$ A , $Fe^{3+} = 0.64$ A , $O^{2-} = 1.45$ A

Interatomic distances

(i) Calculated from crystal structure

Fe - O = 1.958

Fe - Na = 3.18

Na - O = 2.49

(ii) Sum of ionic radii

Fe - O = 2.09

Fe - Na = 1.59

Na - O = 2.4

C. Electronegativities

[redacted]

O = 3.45

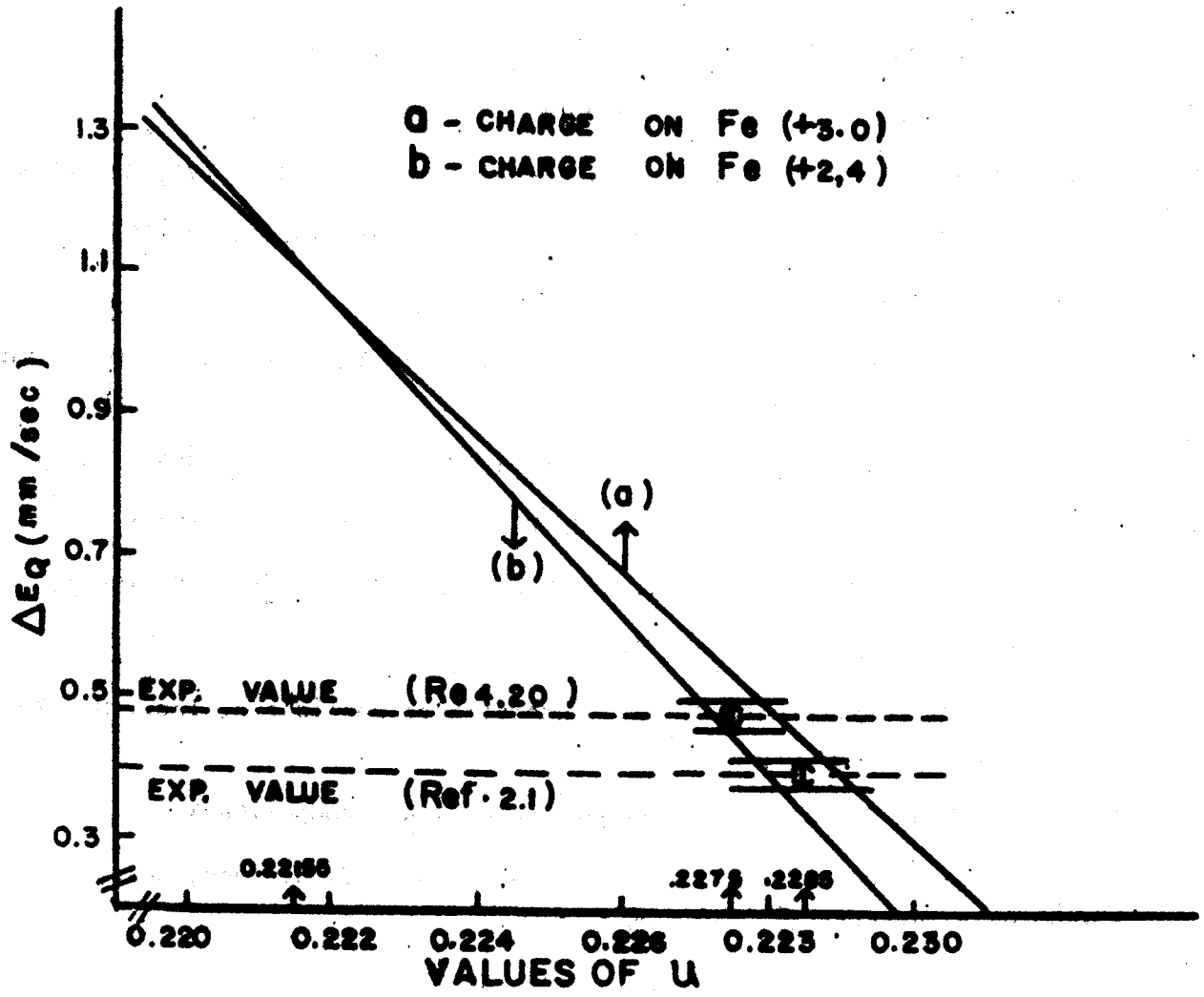

FIG.1 - Quadrupole splitting vs. u parameter in α-$NaFeO_2$

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