

Electric field gradients in niobium pentachloride dimer

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Abstract. Electric field gradient tensors at the bridging chlorine sites in niobium pentachloride dimer have been evaluated using point-charge model with de Wette's plane-wise summation method for rapid convergence of the lattice sums. The results are discussed based on the experimental results and the existing theory on dimeric molecules.

Keywords. Electric field gradients; point-charge model; plane-wise summation method; niobium pentachloride dimer

1. Introduction

Nuclear quadrupole interactions have been studied experimentally in a number of metal halides. But, no theoretical model to date could explain the experimental results satisfactorily. However, ever since the work of Bersohn (1958), the calculations on the electric field gradients (EFG) in several ionic crystals using various models, are reported in the literature. The present work is on niobium pentachloride (NbCl_5) dimer. Here the EFG components of the two bridging chlorines are calculated using the point-charge model with de Wette's plane-wise summation method (de Wette and Schacher 1965) for rapid convergence and the results are discussed.

2. Details of calculations

Niobium pentachloride belongs to the monoclinic class (Zalkin and Sands 1958) with the space group $B_{2/m}$ (first setting*). There are twelve molecules per unit cell with

$$a = 18.30 \pm 0.01 \text{ \AA}; \quad b = 5.888 \pm 0.004 \text{ \AA},$$

$$c = 17.96 \pm 0.02 \text{ \AA} \text{ and } \gamma = 90.6^\circ \pm 0.01^\circ.$$

The unit cell possesses two inequivalent niobium atoms and nine inequivalent chlorines which form into two types of molecules with different symmetries, namely $2/m$ and m as shown in figure 1.

*Though the crystal structure originally is given with respect to the second setting, all the results in the present work are given in first setting only in accordance with the computer program (Dickmann 1966).

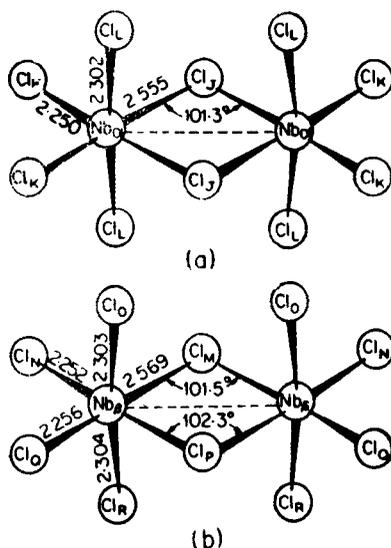


Figure 1. Crystal structure of NbCl_5 dimer molecule with a. $2/m$ symmetry and b. m symmetry.

The expressions for the lattice field gradients consist of conditionally convergent series. These expressions are of the general form

$$\sum_{\lambda} f(x_{\lambda,j}, y_{\lambda,j}, z_{\lambda,j}) r_{\lambda,j}^{-3}$$

where $x_{\lambda,j}$, $y_{\lambda,j}$ and $z_{\lambda,j}$ are the cartesian coordinates of the lattice vector $\hat{r}_{\lambda,j}$ of the point charge j in the cell λ and f is some simple, dimensionless function of its arguments. The conditionally convergent series is slowly convergent, consequently, unfavourable for direct numerical computations. However, the procedure of plane-wise summation of de Wette and Schacher (1965) leads to a rapidly converging expression for the sum. The plane-wise summation means that a summation over λ_1 and λ_2 in the plane $\lambda_3 = 0$ will be carried out first, then in the planes $\lambda_3 = \pm 1$ etc. In short the λ_1, λ_2 summation should be carried out before the λ_3 summation. Here $\lambda_1, \lambda_2, \lambda_3$ are the components of the lattice translation vector $\hat{r}_{\lambda} = \lambda_1 \hat{a} + \lambda_2 \hat{b} + \lambda_3 \hat{c}$ where $\lambda_1, \lambda_2, \lambda_3 = 0, \pm 1, \pm 2 \dots$ etc.

The principles involved in bringing the lattice sums into rapidly converging series and the expressions for the electric field gradient tensor derived for a general triclinic system, but expressed with reference to an unambiguous choice of an orthogonal coordinate system have been given in detail by de Wette and Schacher (1965) and are therefore not repeated here. The orthogonal coordinate system (x, y, z) is chosen such that the x -axis coincides with the crystallographic a -axis, y -axis lying in the ab plane and z -axis perpendicular to xy plane.

A computer program written by Dickmann (1966) in the FORTRAN 60 language for CDC 1604 computer has been used to evaluate the lattice sum by CDC 3600 computer (TIFR Bombay). The lattice sums have been computed for all the niobium and chlorine sites. Unfortunately, convergence is achieved for the lattice sums, only for the

two bridging chlorine atoms M and P of the m -symmetry (figure 1). Convergence of the summations for other sites could not be tried after a stage due to financial constraints and computer time.

As $NbCl_5$ is fairly ionic, by taking the charges $+5$ on Nb and -1 on Cl, the field gradient components at both the bridging chlorine sites are evaluated with respect to the x, y, z system and are given in tables 1 and 2. The EFG components of the rest of the lattice obtained by deducting the intramolecular point charge contributions from the total lattice contributions are also given in the table. The principal components for the three types of contributions and the corresponding values of frequency and the asymmetry parameter (η) which are calculated, using the values of γ_∞ (Burns and Wikner 1961) and Q for ^{35}Cl as -10 and -0.085 barns respectively are presented in table 3. The orientations of the various principal systems (xyz) with respect to the orthogonal (xyz) coordinate system are given in table 4.

Table 1. Field gradient components for total lattice and (rest of the lattice) in $NbCl_5$ for chlorine atom M expressed in ($e \times 10^{24}$ esu).

-0.30362 (-0.59053)	-0.31327 (-0.63858)	0
-0.31327 (-0.63858)	-0.09343 (-0.21364)	0
0	0	0.39705 (0.80417)

Table 2. Field gradient components for the total lattice and (rest of the lattice) in $NbCl_5$ for the chlorine atom P expressed in ($e \times 10^{24}$ esu).

-0.36189 (-0.71081)	-0.27666 (-0.58411)	0
-0.27666 (-0.58411)	-0.05380 (-0.13197)	0
0	0	0.41569 (0.84278)

Table 3. Principal components, frequency and asymmetry parameter from chlorine atom M (atom P).

Due to	q_{XX}	q_{YY}	q_{ZZ}	ν (MHz)	η
Total lattice	0.13191 (0.10881)	0.39705 (0.41569)	-0.52896 (-0.52450)	8.963 (9.011)	0.501 (0.585)
Rest of lattice	0.26373 (0.23049)	0.80417 (0.84279)	-1.06790 (-1.07328)	18.109 (18.393)	0.506 (0.571)
Intramolecular bonding	-0.13224 (-0.12239)	-0.40715 (-0.42709)	0.53939 (0.54948)	9.152 (9.391)	0.509 (0.554)

Table 4. Orientations of principal EFG systems with respect to the xyz system for site M (site P) for various contributions.

Due to	q_{XX}	q_{YY}	q_{ZZ}
Total lattice	54·27°, 144·27°, 90° (59·55°, 149·55°, 90°)	90°, 90°, 0° (90°, 90°, 0°)	35·73°, 54·27°, 90° (30·45°, 59·55°, 90°)
Rest of the lattice	53·22°, 143·22°, 90° (58·18°, 148·18°, 90°)	90°, 90°, 0° (90°, 90°, 0°)	36·78°, 53·22°, 90° (31·82°, 58·18°, 90°)
Intramolecular bonding	52·19°, 142·19°, 90° (56·88°, 146·88°, 90°)	90°, 90°, 0° (90°, 90°, 0°)	37·81°, 52·19°, 90° (33·12°, 56·88°, 90°)
Crystal structure	52·51°, 142·51°, 90° (56·43°, 146·43°, 90°)	90°, 90°, 0° (90°, 90°, 0°)	37·49°, 54·51°, 90° (33·56°, 56·43°, 90°)

3. Results and discussion

Reddoch (1961) reported only one ^{35}Cl resonance line at 13·0581 MHz at 296·5 K and assigned it to the bridging chlorine (J) of the molecule with $2/m$ symmetry. Later Okubo and Abe (1979) observed a multiple spectrum of chlorine resonance at 77 K. Okubo (1982) separated these lines into three distinct groups with average frequencies 6·97, 7·44 and 13·31 MHz and assigned them to axial (L), equatorial (K) and bridging (J) chlorines respectively, of the molecule with $2/m$ symmetry. However, since the two molecules of different symmetries appear to be identical, the frequencies of the three bridging chlorines (J , M , P) will be very close. So the frequency of the bridging chlorine (J) should be of the same order and closeness as the two calculated frequencies of M and P chlorines. Thus the fair agreement of the calculated frequencies (see table 3) with the experimental frequency of J chlorine finds its justification.

It is interesting to note from table 3 that the principal components of the total lattice are the algebraic sum of the components of the intramolecular and the rest of the lattice field gradients. In magnitude, the maximum contribution to the total lattice principal Z component comes from the rest of the lattice, but it is reduced to half, due to the intramolecular contribution (point-charge model). In a way, this supports the ionic nature of the compound.

By studying the electronic structure of some of the group III dimeric halides ($M_2 X_6$), Casabella *et al* (1959) derived the relation between η of the metal (M) or bridging halogen (X) atoms and the angle ξ between the lobes in the bonding wave functions as $\eta = -3 \cos \xi$, under two assumptions, (a) the molecule possesses $m m m$ symmetry (b) the principal Z axis is normal to $M X M$ plane and the principal X axis is along the internal bisector of $M \hat{X} M$.

In the absence of the experimental value for η , the angles (ξ) are calculated applying the above relation for the NbCl_5 dimer and using the values of η from table 3 and they range from 99·6° to 101·2° which are in good agreement with bond angles from crystal structure (figure 1). The maximum deviation occurred is less than 2°. Further, it can be seen from table 4 that the orientations of the principal systems for both sites agree with those derived from crystal structure for dimeric molecule under assumption (b). The orientations came out to be nearly the same for all the three

types of contributions. Therefore, the point charge calculations in general predict the orientations of the principal systems correctly.

The agreement of orientations of the principal systems and the values of angle ξ from the relation of Casabella *et al* (1959) and the assumptions involved enable us to state that the first assumption is not so critical, as the molecule of NbCl_5 possesses m and $2/m$ symmetries. In GaCl_3 dimer (Peterson and Bridenbaugh 1969; Satyanandam 1974) also, the results are in good agreement, although the true symmetry of the molecule is $\bar{1}$.

In conclusion, the high value of η and the low value of the NQR frequency in NbCl_5 , which are the general characteristics of an ionic compound, and the agreement of the various calculated quantities from the point-charge model, with the experimental frequency and the predicted values of the other NQR parameters are consistent with the ionic nature of NbCl_5 .

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