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Quadrupole Interactions in Chrysoberyl*

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The electric field-gradient tensor has been computed using the point multipole model at the two inequivalent Al sites and at the Be site in chrysoberyl crystal. The calculated asymmetry parameters, the orientation of the principal field-gradient axes, and the quadrupole coupling constants are compared with values obtained from NMR measurements on the single crystal. The oxygen-dipole contributions to the field gradients are found to be very sensitive to the assumed oxygen polarizability. As the exact value is not known, calculations are carried out for three values: 2.19, 1.34, and 1.0 Å^3, the former two have been used in earlier investigations on Al_2O_3 and BeO. The results for the three polarizabilities are discussed in the light of experimental observations. The deviations between calculated and observed values of the quadrupole-interaction parameters appear to decrease as the oxygen polarizability is varied from 2.19 to 1.0 Å^3, and best over-all agreement is obtained for $\alpha = 1.0$ Å^3.

1. INTRODUCTION

THE computation of electric field gradients has been of growing interest in recent years. All experiments on nuclear quadrupole resonance (NQR), nuclear magnetic resonance (NMR), and the Mössbauer effect yield a value of the quadrupole coupling constant eQq, where Q is the quadrupole moment of the nucleus, and q is the electric field gradient. Neither Q nor q is observed directly. In some cases, Q is obtained by observing eQq in a particularly simple solid for which q at the nucleus can be calculated in a reliable manner. On the other hand, if Q is available from an independent source, say atomic-beam electric- or magnetic-resonance experiments, q can be calculated in crystals for which NQR has been observed. The observed value of q so obtained could be used to investigate the validity of various models for the distribution of electric charge in ionic crystals. Because of the complexities associated with more sophisticated and probably more realistic models, most field-gradient calculations on ionic solids are based on the point-charge model. However, even such a simple model presents serious difficulties. In an ideal ionic crystal, the field gradient arises solely from charges and dipoles external to the ion, except for the polarization produced in the ion by this field gradient. The effective field gradient has been shown[1] to be $(1-\gamma_\infty)q_{\text{ext}}$, where γ_∞ is the antishielding factor of the ion. In spite of its approximate nature, the point-multipole model is often invoked with varying degrees of success to explain the observed quadrupole interactions and the optical and magnetic-resonance data on transition-metal[2,3] and rare-earth[4] ions in a variety of host crystals.

Most of the field-gradient calculations in the literature[2,3] were carried out on crystals with axial symmetry, i.e., the asymmetry parameter $\eta=0$. The only experimental data available for comparison are the quadrupole-coupling constants. Hence, from the calculated electric field gradients, the quadrupole coupling constant $(1-\gamma_\infty)\ eqQ/h$ is computed and compared with the observed value. However, this parameter contains two quantities: the quadrupole moment Q of the nucleus and the antishielding factor γ_∞ of the ion. Quadrupole moments of some of the nuclei are not known very accurately. The value of γ_∞ is often uncertain,[5] although fairly accurate theoretical values exist for the free ions. Thus the quadrupole coupling constant may not be considered a good parameter for comparison, particularly when one is interested in checking various models of charge distribution in crystals. Further, most of the calculations were on crystals for which x-ray diffraction data were old, and hence no definite conclusions could be drawn, as the calculated field gradients are very sensitive to the atomic-position parameters. Only in two of the cases recently studied, Fe_2O_3,[3] and BeO,[6] could the point-multipole model be successfully used to explain quadrupole interactions. Nicholson and Burns[7] also obtained reasonable agreement between measured and calculated values of eqQ of Fe^{3+} in several rare-earth iron garnets for the octahedral sites. However, at the tetrahedral sites in the same crystals, the agreement is poor, which has been ascribed to effects of covalency.

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The only attempt to check the point-charge model using observed parameters which are independent of Q and γ_∞ was carried out by Belford *et al.*[8] using spodumene and beryl. However, no definite conclusions could be drawn because: (1) the atomic-position parameters in the crystal are not known accurately, and (2) the contribution of induced dipoles was not considered.

2. PURPOSE OF THE PRESENT INVESTIGATION

It may be noted that beryl and spodumene are silicates of layer structure where the ionic model may not be a good approximation. When one is interested in checking models of charge distribution, the resonance frequency is not a reliable parameter for comparison. A better check is provided by values of the asymmetry parameter and orientation of the principal axes of the electric field-gradient tensor, as these are independent of Q and γ_∞.

Chrysoberyl offers an ideal case for a thorough investigation of this type. NMR experiments on the single crystal have been carried out by Hockenberry *et al.*,[9] and the quadrupole coupling constant, asymmetry parameter, and orientation of the principal axes were reported for the two inequivalent Al sites. Similar data for the Be site are also available from recent experiments by Reaves and Gilmer[10] on the single crystal. Thus a total of 12 observed parameters are available to us on the crystal. Of these, nine are independent of γ_∞ and Q: three asymmetry parameters, one each for the Al(1), Al(2), and Be sites; one angle specifying the orientation of the principal axes[11] for the Al(1) site, three angles for the Al(2) site, and one for the Be site; and finally the ratio of the two quadrupole coupling constants of Al(1) and Al(2) sites. The other three parameters—quadrupole coupling constants of Al(1), Al(2), and Be—are dependent on γ_∞ and Q. The atomic-position parameters are available from the x-ray diffraction work of Bragg and Brown.[12] An accurate revised analysis of the lattice parameters is also available from recent experiments of Farrell *et al.*[13] In spite of the diffuseness of the O^{--} charge distribution, the compactness of the positive ions as manifested by their small radii argues against the possibility of much covalent bonding. Hence, a detailed study of the quadrupole interactions of Al^{27} and Be^9 has been carried out, and the results are presented in this article.

3. CALCULATIONS AND RESULTS

The mineral chrysoberyl is a hard dense gemstone with interesting optical properties. It is a hexagonal close-packed analog to the cubic close-packed spinel structure. Its structure is isomorphous to olivine, $(MgFe)_2SiO_4$. The oxygens form a distorted hexagonal close-packed array in which one-eighth of the tetrahedral interstices are occupied by beryllium, and the octahedral sites are filled by aluminum. The hexagonal close-packing of the oxygen atoms is brought out by the fact that a perfect packing requires for its description an axial ratio 0.471:1:0.577. In chrysoberyl this ratio is 0.4707:1:0.5825. The lattice parameters were determined accurately by Swanson *et al.*[14] and are given as $a=4.427$, $b=9.404$, and $c=5.476$ Å.

The space group is Pb_{nm}, orthorhombic with four molecules in the unit cell. The aluminum ions are all octahedrally coordinated, but occupy sites of two different symmetries. Al(1) sites are on reflection planes with position parameters $\pm(u, v, \frac{1}{4}, \frac{1}{2}-u, v+\frac{1}{2}, \frac{1}{4})$ with $u=0.00595$ and $v=0.27319$. O(1) and O(2) oxygen ions also lie on the mirror planes with $u=0.79106$, $v=0.09051$, and $u=24097$ and $v=0.43343$, respectively. Al(2) ions occupy a set of inversion centers at $(0, 0, 0)$, $(0, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. O(3)-type oxygens are located in the general positions at (x, y, z) ,$(x+\frac{1}{2}, \frac{1}{2}-y, \bar{z})$, $(x, y, \frac{1}{2}-z)$, $(x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2})$ with $x=0.25850$, $y=0.16318$, and $z=0.01718$. Be ions also lie on the reflection planes with $u=0.43347$ and $v=0.09204$.

The general method of calculation followed is the same as that reported by Narasimha Rao and Narasimha Murty.[15] The xyz coordinate system is conveniently chosen to coincide with the crystalline abc axes, with x parallel to a, y parallel to b, and z parallel to c. As the oxygen ions are very deformable, the induced dipole moments may be considerable and give significant contribution to the field gradients. The polarizabilities[16] of the two metallic ions Al and Be are small (0.05 and 0.008 Å^3, respectively), and hence the induced moments in these ions can safely be neglected. The four O(1)-type oxygens are equivalent, as are the four O(2)-type oxygens and the eight O(3)-type oxygens. However the relative signs of the electric fields, and hence the induced dipole moments, are different, depending upon the environment. Let μ_x, μ_y be the effective-dipole moment components in Debye units for O(1)-type oxygens; M_x, M_y for O(2)-type oxygens; and ν_x, ν_y, ν_z for O(3). As O(1)- and O(2)-type oxygens are on reflection planes perpendicular to the c axis, the z components of induced moments vanish.

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TABLE I. Induced dipole moments of oxygen ions for various polarizabilities (Debye units).

Type of oxygen	Dipole-moment component	Polarizability in Å^3 $\alpha=2.19$	$\alpha=1.34$	$\alpha=1.0$
O(1)	μ_x	-0.899	-0.659	-0.531
	μ_y	0.116	0.277	0.279
O(2)	M_x	-0.168	-0.211	-0.185
	M_y	-1.433	-1.102	-0.904
O(3)	ν_x	0.643	0.398	0.308
	ν_y	1.300	0.899	0.726
	ν_z	-1.240	-0.854	-0.676

Looking at the crystal structure, the relative signs of the induced moments for various ions can be written down.

In order to estimate the dipole moments, it is necessary to calculate the electric field at O(1), O(2), and O(3) sites. Since the dipoles themselves contribute to the electric field, the dipoles must be calculated self-consistently. Thus, the dipole component $M_i(i=x, y, z)$ is obtained:

$$M_i=\alpha(F_{ci}+F_{\mu i}), \tag{1}$$

where F_c is the field due to charges, F_μ is the field due to dipoles, and α is the polarizability of O^{--} ions. F_μ contains the variables μ, M, and ν. The x, y, and z components of the field are calculated.

The components of the electric field at any point due to ideal point charges (F_c) and point dipoles (F_μ) located at all the neighboring ions are calculated using the equations reported by Rao and Murty.[15]

There are various methods in the literature for the calculation of the lattice sums. The internal fields and field gradients in dipole lattices have been calculated by DeWette and Schacher.[17] Rapidly converging expressions for the conditionally convergent dipole sums are obtained by the method of planewise summation involving, in part, summation over the reciprocal lattice. Artman and Murphy[2] criticized the procedure because it is usually not convergent for inverse powers of R smaller than the fourth. They have used a method proposed by Wood[18] for calculation of the Madelung constants in crystals of low symmetry. The ions are grouped[19] into molecules of zero electrical charge; then the summation proceeds over arrays of molecules. (Several procedures for performing the grouping have been proposed in the literature. Madelung,[19] who was the first to undertake a thorough study of the problem, collected the ions into groups forming linear elements inside the crystal. Ewald[20] carried out part of the calculation in the reciprocal space and was thus able to obtain rapid convergence. In the Evjens method,[21] later modified by Dahl,[22] the groups are made up of ions situated in the same unit cell. Procedures suggested by Hojendahl,[23] Frank,[24] Roy,[25] Kanamori *et al.*,[26] and Nijboer and DeWette[27] are similar.) This procedure allows the presence of surface effects to be ignored. Wood in his examples found that the rapidity of convergence depends on the method used to group the cells. Grouping by shells or layers about the central cell containing the reference ion was found more effective than grouping the cells according to their contribution to the energy.

We have found it more convenient to obtain the lattice sums in real space, considering all ions within a sphere of appropriate radius R. Recourse to a reciprocal-lattice summation would have given convergence for much lower values of R than those we used. However, since there are a number of lattice sums to be evaluated in this investigation, and since there are a large number of ions in the unit cell, the necessary structure factors for the reciprocal-lattice summation would be rather complex. We have checked the convergence by performing the summations for $R=50$ Å and $R=100$ Å. The convergence is found to be good. Lattice sums for the field due to dipoles and the field gradient due to charges (both going as $1/R^3$) and the field gradient due to dipoles ($1/R^5$ dependence) are calculated for $R=50$ Å. However, for the field due to charges ($1/R^2$ dependence), it has been found necessary to go up to $R=100$ Å. Lattice sums in this case are calculated for $R=100$ and 110 Å (the latter includes the contribution of a large number of additional ions, of order 10^5), and the values agreed within a few parts per thousand. All the other lattice sums are more accurate. The field due to dipoles and field gradients due to charges are given by the same lattice sums. Hence, both are obtained in one program. All the computations were carried out on the CDC-3600A high-speed computer of the Tata Institute, Bombay.

Assuming the polarizability of O^{--} ions $\alpha=2.19$ Å^3, the same value used by Taylor and Das[6] in BeO, a set of linear equations of type (1) are formulated and solved by the method of postmultiplication,[28] and the dipole-moment components μ_x, μ_y, M_x, M_y, etc., are obtained. The values are given in Table I.

Thus a model is set up by assigning each lattice point the corresponding charge and dipole moment, and both these contribute to the field gradients. The general formulas for computing the field gradients are the same as those used by Rao and Murty.[15] The complete field-

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TABLE II. Contribution of charges and dipoles to the electric field-gradient tensor.

Site	Field-gradient component	Charge contribution ($10^{-24}e$ esu)			Dipole contribution (10^{14} esu)			Total (10^{14} esu)		
		Al^{3+}	O^{--}	Be^{++}	$\alpha=2.19$	$\alpha=1.34$	$\alpha=1.0$	$\alpha=2.19$	$\alpha=1.34$	$\alpha=1.0$
Al (1)	q_{xx}	−0.0814	0.1312	−0.0332	0.6495	0.4695	0.3815	0.7295	0.5495	0.4616
	q_{yy}	0.1362	−0.1599	0.0923	−1.6097	−1.0684	−0.8468	−1.2770	−0.7357	−1.5141
	q_{zz}	−0.0555	0.0287	−0.0592	0.9602	0.5989	0.4654	0.5474	0.1861	0.0526
	q_{xy}	0.0105	−0.0375	−0.0642	0.6369	0.5554	0.4726	0.1983	0.0170	−0.0658
Al (2)	q_{xx}	−0.3433	0.0610	0.2709	0.0713	0.0386	0.0171	0.0167	−0.0160	−0.0375
	q_{yy}	0.0320	0.1078	−0.2096	0.4974	0.4248	0.2303	0.1672	0.0946	−0.0999
	q_{zz}	0.3112	−0.1689	−0.0623	−0.5689	−0.4634	−0.2474	−0.1839	−0.0786	0.1374
	q_{xy}	0.0015	0.0204	0.0876	−1.0390	−0.6899	−0.2789	−0.7074	−0.3583	0.0527
	q_{yz}	0.0789	−0.2646	0.1446	−1.1198	−0.7770	−0.3102	−1.3163	−0.9739	−0.5067
	q_{zx}	−0.0054	−0.1254	0.1410	−0.8275	−0.5527	−0.2144	−0.7789	−0.5041	−0.1658
Be	q_{xx}	0.3565	−0.5572	−0.0490	−0.0202	0.0217	0.0336	−1.2192	−1.1770	−1.1654
	q_{yy}	−0.2194	0.4098	−0.0181	0.4942	0.3528	0.3153	1.3372	1.1958	1.1583
	q_{zz}	−0.1372	0.1474	0.0671	−0.4740	−0.3744	−0.3489	−0.1180	−0.0184	0.0071
	q_{xy}	0.0210	0.0462	−0.0186	0.0535	0.0709	0.0283	0.2860	0.2222	0.2608

gradient tensors at the Al(1), Al(2), and Be sites are obtained in the *xyz* system. The trace of the tensors, $q_{xx}+q_{yy}+q_{zz}$, is 0 to within a few parts in a thousand. The contributions of the charges and induced dipoles to the electric field-gradient tensor for the three sites are shown in Table II. It may be observed that the contribution of the induced dipoles is significant.

Al(1) and Be are on mirror planes perpendicular to the crystal *c* axis, and hence *c* is a principal axis for these two sites. The matrices are easily diagonalized and their principal values obtained. These are shown in Table III. The principal values are designated according to the convention that q_{ZZ} is maximum, so that the quadrupole coupling constant is given by $eQq_{ZZ}(1-\gamma_\infty)/h$ and the asymmetry parameter $\eta=|q_{XX}-q_{YY}|/q_{ZZ}$. In the calculation of the quadrupole coupling constant, the quadrupole moments of Al and Be are assumed[29] to be 0.149 and 0.05 b respectively. Theoretical values[30] of the antishielding factors, −2.59 for Al^{+++} and 0.185 for Be^{++}, are used. The calculated values of the coupling constants along with the observed values[9,10] are presented in Table IV.

The comparison between the observed and calculated values does not seem to be encouraging, particularly for the Al sites when the induced dipoles are calculated using the value of 2.19 $Å^3$ for the polarizability of oxygen ion. In the case of Be, though the asymmetry parameter and quadrupole coupling constant agree approximately with the observed values, the orientation of the principal axes does not conform to the observations (see Table V).

We now examine the various uncertainties in the calculation. As the crystal structure is a recent determination and the parameters are supposed to be accurate, we may look into the other factors. One of the uncertain parameters seems to be the value of the polarizability of the oxygen ions in the particular crystal. Taylor and Das[6] used a value of 2.19 for the BeO crystal, and Sharma and Das[3] used the same value for corundum, whereas Artman and Murphy[2] preferred a value of 1.34 for that crystal. To investigate the effects of this parameter on the final results, we have repeated the calculation for $\alpha=1.34$ $Å^3$. These results are also shown in Tables I–IV. It may be observed that the

TABLE III. Electric field-gradient tensor in the principal-axes system (in units of 10^{14} esu).

	$\alpha=2.19$			$\alpha=1.34$			$\alpha=1.0$		
Al(1)	0.5474	0	0	0.1861	0	0	0.0526	0	0
Site	0	0.7493	0	0	0.5495	0	0	0.4617	0
	0	0	−1.2963	0	0	−0.7355	0	0	−0.5143
Al (2)	0.5900	0	0	0.2784	0	0	−0.0717	0	0
Site	0	1.3200	0	0	0.9917	0	0	−0.5103	0
	0	0	−1.9100	0	0	−1.2702	0	0	0.5820
Be	−0.1186	0	0	−0.0184	0	0	0.0071	0	0
Site	0	−1.2500	0	0	−1.1980	0	0	1.1870	0
	0	0	1.3685	0	0	1.2160	0	0	−1.1941

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TABLE IV. Calculated and observed values of quadrupole coupling constant and asymmetry parameter.

ion	Q (barns)	$1-\gamma_\infty$	η_{calc}			η_{obs}	$eqQ(1-\gamma_\infty)/h$ (Mc/sec) calculated			
			$\alpha=2.19$	$\alpha=1.34$	$\alpha=1.0$		$\alpha=2.19$	$\alpha=1.34$	$\alpha=1.0$	obs
Al(1)	0.149	3.59	0.16	0.50	0.80	0.76	5.07	2.88	2.00	2.846
Al (2)	0.149	3.59	0.40	0.57	0.75	0.94	7.46	4.96	2.26	2.850
Be	0.05	0.815	0.83	0.97	0.98	0.90	0.40	0.36	0.35	0.318

dipole contributions to the field gradients are very sensitive to the assumed value of the polarizability.

It is encouraging to observe that there is a tendency for the calculated values of the asymmetry parameter (as well as the quadrupole coupling constant) to come closer to the observed values for the three sites Al(1), Al(2), and Be. The agreement may not be considered satisfactory, even in this case, for the Al sites. In view of the uncertainty of the value of α in the crystal under consideration, we propose to examine the possibility of whether any reasonable value of α might consistently explain all the observed parameters.

To have some idea of the nature of the variation in the final results, we have calculated the approximate dipole contribution to the field gradients for several values of α close to but less than 1.34 Å^3 by linear extrapolation of the results for $\alpha=2.19$ and 1.34 Å^3. The contribution of the charges, of course, does not vary. The results are found to be encouraging, and seem to indicate that for $\alpha\simeq 1.0$ A^3 we might succeed in explaining all the observed parameters. Hence an exact calculation was undertaken for $\alpha=1.0$ Å^3. These results are also shown in Tables I–IV.

4. DISCUSSION

It may be observed from Table IV that the calculated asymmetry parameters for Al(1) and Al(2) get closer to the observed values as the oxygen-dipole polarizability is varied from 2.19 to 1.0 through 1.34 A^3. The calculated quadrupole coupling constants exhibit similar behavior, except for the Al(1) value for $\alpha=1.34$, which agrees better with experiment than the value for $\alpha=1.0$. The theoretical ratio (0.9) of the Al(1) to the Al(2) coupling constant for $\alpha=1.0$ is close to the experimental value (1.0), and agrees better than the individual values for Al(1) and Al(2). The observed coupling constants for the two sites may be obtained almost exactly for an antishielding factor $(1-\gamma_\infty)=4.8$ for Al^{3+} in the crystal, which is not too far from the theoretical free-ion values 3.59 due to Das and Bersohn[30] and 3.31 due to Burns.[31]

In the case of Be, the total field gradients are less sensitive to the oxygen polarizability, because the dipole contributions are much smaller than the charge contributions. (The charge and dipole contributions to q_{zz} are about the same in magnitude but opposite in sign, with the result that the total value is small and again insensitive to the assumed polarizability.) The theoretical asymmetry parameters for the three polarizabilities are within 10% of the experimental value. Similarly, the quadrupole coupling constants for the three polarizabilities are not far from the observed value, the value for $\alpha=1.0$ being nearer. The theoretical antishielding factor of Be^{++} explains the observed coupling constant quite satisfactorily.

The orientation of the principal field-gradient axes for the three polarizabilities are computed for the Al(1), Al(2), and Be sites and are presented in Table V. The observed values are listed in angles for the Al(1), Al(2) sites by Hockenberry *et al.*[9] and for the Be site by Reaves and Gelmer,[10] and we have given the corresponding direction cosines for comparison in the table. The angles are also shown in parentheses, as they give a convenient physical picture. The *abc* axes given by Hockenberry *et al.* correspond to our *cba* axes, and their values are transformed accordingly. Reaves and Gelmer's axes system is the same as ours.

For Al(1), the calculated minimum field gradient q_{XX} lies along the crystal c axis for all the three polarizabilities; this is also borne out by experiment. However, the calculated orientation of the other two principal axes does not conform to the observations for any of the three polarizabilities. The maximum field gradient q_{ZZ} lies in the ab plane closer to the a axis, and the intermediate value q_{YY}, also in the ab plane, is closer to the crystal b axis, in agreement with experiment. There are four ions of the Al(1) type in the unit cell, two identical ions in each of two equivalent sites. The magnitude of the gradient is the same for both the sites, but the relative orientations are different. Symmetry considerations show that c is a principal axis for both sites, and the orientation of each of the remaining two principal axes of one set may be obtained from the other by reflection through the bc plane followed by parallel translation. The experimental values indicate that the principal Z axes of the two equivalent Al(1) sites lie on either side of the crystal a axis, making an angle 35° with it, and the principal Y axes lie on either side of crystal b axis, making the same angle 35° with it. The corresponding calculated angles are 6°, 0°, 4° for $\alpha=2.19$, 1.34, 1.0, respectively.

In the case of Al(2), we found that the direction cosines for $\alpha=1.0$ agreed approximately with the observed values if the crystal a axis is altered to $-a$,

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TABLE V. Orientation of the principal field-gradient axes with respect to the crystalline axes.

		Calculated values			Observed values		
				$\alpha=2.19$			
Al (1) site		X	Y	Z	X	Y	Z
	a	0 (90°)	−0.097 (96°)	0.995 (6°)	0 (90°)	0.578 (54.7°)	0.816 (35.3°)
	b	0 (90°)	0.995 (6°)	0.097 (84°)	0 (90°)	0.816 (35.3°)	−0.578 (−54.7°)
	c	1 (0°)	0 (90°)	0 (90°)	1 (0°)	0 (90°)	0 (90°)
				$\alpha=1.34$			
	a	0 (90°)	0 (90°)	1.0 (0°)			
	b	0 (90°)	1.0 (0°)	0 (90°)			
	c	1.0 (0°)	0 (90°)	0 (90°)			
				$\alpha=1.0$			
	a	0 (90°)	0.067 (86°)	0.998 (4°)			
	b	0 (90°)	0.998 (4°)	−0.067 (−86°)			
	c	1 (0°)	0 (90°)	0 (90°)			
				$\alpha=2.19$			
Al (2) site							
	a	−0.878 (−29°)	−0.021 (91°)	−0.479 (−61°)	−0.975 (−12.8°)	0.012 (89.3°)	0.184 (79.4°)
	b	−0.297 (−73°)	−0.758 (−41°)	0.581 (54°)	−0.023 (−88.7°)	0.826 (34.3°)	−0.564 (−55.7°)
	c	−0.376 (−68°)	0.653 (49°)	0.659 (49°)	0.211 (77.8°)	0.555 (56.3°)	0.800 (36.8°)
				$\alpha=1.34$			
	a	−0.893 (−27°)	+0.092 (85°)	−0.440 (−64°)			
	b	−0.369 (−68°)	−0.716 (−46°)	0.595 (53°)			
	c	−0.259 (−75°)	0.693 (46°)	0.672 (48°)			
				$\alpha=1.0$			
	a	−0.958 (−17°)	−0.136 (98°)	0.255 (75°)			
	b	−0.263 (−75°)	0.763 (40°)	−0.590 (−54°)			
	c	0.114 (83°)	0.632 (51°)	0.767 (40°)			
				$\alpha=2.19$			
Be site							
	a	0 (90°)	0.995 (6°)	0.104 (84°)	0 (90°)	−0.148 (98.5°)	0.989 (8.5°)
	b	0 (90°)	−0.104 (96°)	0.995 (6°)	0 (90°)	0.989 (8.5°)	0.148 (81.5°)
	c	1 (0°)	0 (90°)	0 (90°)	1 (0°)	0 (90°)	0 (90°)
				$\alpha=1.34$			
	a	0 (90°)	0.995 (5°)	0.094 (85°)			
	b	0 (90°)	−0.094 (95°)	0.995 (5°)			
	c	1 (0°)	0 (90°)	0 (90°)			
				$\alpha=1.0$			
	a	0 (90°)	−0.110 (96°)	0.994 (6°)			
	b	0 (90°)	0.994 (6°)	0.110 (84°)			
	c	1 (0°)	0 (90°)	0 (90°)			

i.e., if the angles are measured relative to the negative-*a* direction. There are four equivalent Al(2)-type ions in the unit cell. The magnitude of the field gradient is the same at all the four sites, but the principal axes are rotated relative to each other; the orientation at one site can again be obtained from the others by symmetry arguments. From Fig. 2 of Hockenberry *et al.*,[9] we understand that they have given the orientation of the principal axes for the Al(2) ion at $(\frac{1}{2}, \frac{1}{2}, 0)$, whereas our calculations are for the ion at (0, 0, 0) in the lattice. Symmetry considerations indicate that the orientation of the principal axes for the Al at $(\frac{1}{2}, \frac{1}{2}, 0)$ may be obtained from that of the Al at (0, 0, 0) by reflection in the *bc* plane followed by parallel translation. Hence if the principal axis X of the Al at (0, 0, 0) is (l, m, n) in the *abc* system, then the corresponding X' of the Al at $(\frac{1}{2}, \frac{1}{2}, 0)$ is (l, m, n) in the $-abc$ system or $(-l, m, n)$ in the *abc* system. Similar arguments hold for the principal Y, Z axes. The values thus derived, shown in Table V, approximately conform to the observed values. Corresponding values for $\alpha=2.19$ and 1.34 are also shown in Table V. In these cases, the results do not agree with experiment regarding the relative signs or even the magnitudes of the direction cosines; the values for $\alpha=1.0$ appear to be nearer to the experimental values.

In the case of the Be site, the calculated minimum gradient q_{XX} is along the crystal c axis for all the three polarizabilities, and q_{YY}, q_{ZZ} lie in the *ab* plane, in agreement with the experimental observations. The maximum gradient q_{ZZ} is close to b, and the intermediate gradient q_{YY} is close to the a axis for $\alpha=2.19$ and 1.34; whereas for $\alpha=1.0$, q_{ZZ} is close to the a axis and q_{YY} is close to b, in conformity with the experimental result. The general position coordinates of the four Be ions are the same as those of the four Al(1) ions and hence their behavior is similar with respect to the orientation of the principal axes. For the two equivalent Be sites in the crystal, the calculated q_{ZZ} lies at 6° on either side of a axis, and q_{YY} on either side of b, making the same angle 6° with it, which compares well with the experimental angle 8.5°.

It is difficult to speculate on the reasons why the calculations can explain the observed results for the Al(2) site (and also for the Be site), but not for the Al(1) site in the same crystal. Both Al(1) and Al(2) have oxygen octahedrons, the only difference being that the Al(1) ions lie on reflection planes and the Al(2) at inversion centers. The oxygen octahedron of Al(1) is appreciably larger than that of Al(2). The average Al-O bond length is 1.938 Å for Al(1)-type ions and 1.890 Å for Al(2)-type ions, both being close to the average Al-O value 1.915 Å in the similar crystal corundum, which indicates that the chemical bonding may be similar in the two crystals. It may be mentioned that in the case of corundum calculations both by Artman and Murphy[2] and by Sharma and Das[3] indicate a significant deviation of the calculated quadrupole coupling constant of Al from the observed value which could not be explained by reasonable variation of the antishielding factor. Perhaps some kind of cancellation of the effects of overlap and covalency is taking place at Al(2) sites because they are at inversion centers, and this results in the agreement. The contribution of induced quadrupoles, not considered here, may alter the calculated results. Further, the dipole polarizability to be used for calculating the induced dipoles of oxygen ions in the crystal is not known exactly. However, a significant feature of this detailed study is that it has been found possible to explain 11 out of the 12 observed parameters, assuming the oxygen polarizability as 1.0 Å^3 in the crystal. The optical polarizability for O^{--} in Al_2O_3 was reported by Tessman, Kahn, and Shockley[32] as 1.3 Å^3, but Taylor and Das[6] showed that the polarizability of O^{--} to be used for calculations of induced dipoles is different from the optical polarizability. In their calculations for BeO they obtained a value 2.19 Å^3 using the results of the pressure variation of the dielectric constant, as compared to the optical polarizability 1.29 Å^3. In the absence of such pressure measurements for Al_2O_3, Sharma and Das[3] used a value 2.19 Å^3 which they obtained for BeO. On the other hand, Artman and Murphy[2] suggest that the Tessman value is quite appropriate in corundum, and they used 1.34 Å^3 in their calculations. It may be mentioned that the deviation between the calculated and the observed quadrupole coupling constant for Al^{27} in corundum is less for Artman and Murphy's results than for Sharma and Das's. Tessman *et al.*[32] reported a spread of 0.5 to 3.2 Å^3 for the oxygen polarizability in various crystals. It would be interesting to carry out detailed investigations, such as of the pressure variation of the dielectric constant, to fix the value uniquely in the crystal.

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[32] J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **82**, 890 (1953).