

sorption data for the same experimental conditions as described here for SnS_2 . More extensive measurements in the infrared wavelength region are being carried out to identify a free-carrier-absorption mechanism in SnSe_2 and its correlation to carrier concentration.

Note added in manuscript. A report on the present investigation was recently given by Itoga *et al.*¹⁸ Subsequent to this report, Greenaway and Nitsche¹⁹ have published optical data on several C6-type compounds including some absorption data for SnS_2 in the low-absorption region. The general profile of their absorption curve appears to be in good agreement with that obtained in the present investigation. However, in the

¹⁸R. S. Itoga, G. Domingo, and C. R. Kannewurf, *Bull. Am. Phys. Soc.* **10**, 681 (1965).

¹⁹D. L. Greenaway and R. Nitsche, *J. Phys. Chem. Solids* **26**, 1445 (1965).

analysis of the photon energy dependence for the indirect-transition mechanism a preference for a quadratic dependence on energy is shown with more than a single slope indicated. Such structure was not observed in the present investigation. Their mean value for E_g' of 2.21 eV is slightly greater than the corresponding value of 2.07 eV determined here. Absorption data for $\alpha > 10^4 \text{ cm}^{-1}$ were not presented so that a comparison of results in the direct-transition region could not be made.

ACKNOWLEDGMENTS

The authors would like to thank Professor A. W. Ewald for supplying the high-purity tin used in the crystal synthesis and Professor M. E. Brodwin for the use of his magnetic-field equipment.

Electric Field Gradient Calculations in Transition-Metal Sesquioxides

J. O. ARTMAN

Departments of Physics and Electrical Engineering, Carnegie Institute of Technology, Pittsburgh, Pennsylvania

(Received 1 September 1965)

We present computations of the electric field gradient at the cation sites in the Cr, Fe, Ti, and V sesquioxides isomorphous to corundum. We include dipolar as well as monopolar contributions. Except for $\alpha\text{-Fe}_2\text{O}_3$ we find that the dipolar and the monopolar field-gradient contributions are opposite in sign and roughly of the same order of magnitude. In so far as existing data permit, we have used these tabulations to determine the electric nuclear quadrupole moment (Q) of the odd isotopes. The Q values found here seem to be somewhat larger than the results of others. In the cases of Cr^{53} and V^{51} existing data are such that only $|Q|$ can be determined. Our calculation for Al^{27} has been given previously. In $\alpha\text{-Fe}_2\text{O}_3$ the dipolar field-gradient term has the same sense as the monopolar, and is comparatively small. We find $Q(\text{Fe}^{57m})$ to be 0.41 b. A recent $\alpha\text{-Fe}_2\text{O}_3$ field-gradient calculation which yielded a $Q(\text{Fe}^{57m})$ value of 0.277 b is believed to be in error.

INTRODUCTION

WE present in this paper the results of computations of the electric field gradient at the cation sites in a number of transition-metal sesquioxides.¹ Crystallographically, the structures considered (those of Cr, Fe, Ti, and V) are isomorphous to $\alpha\text{-Al}_2\text{O}_3$ (corundum). We include the presence in the lattice of point dipoles as well as point monopoles. In view of the nuclear quadrupole data which increasingly are becoming available we believe that such field-gradient evaluations are of current interest. In the cases of Cr^{53} and V^{51} we are able to evaluate only the absolute value of the nuclear quadrupole moment Q ; in the case of Fe^{57m} we evaluate both the magnitude and sign. Our previous results for Al^{27} are also listed.

The corundum lattice can be decomposed into a sequence of bipyramids, each consisting of three O^{2-}

ions located on the vertices of an equilateral triangle with the trivalent cations disposed above and below.² (See Fig. 1.) From symmetry, both the electric field and the electric field gradient at a cation site must lie along the hexagonal (c) axis. The fields at the O sites lie in the basal plane (perpendicular to the c axis) and are directed along the bisectrices of the oxygen triangles.

At a cationic position the field gradient $q_{X'}$ can be written as the sum

$$q_{X'} = q_m' + q_{a-X'} p_X + q_{a-O'} p_O, \quad (1)$$

where q_m' is the usual monopolar contribution; $q_{a-X'}$, $q_{a-O'}$ are the normalized contributions from the dipoles at the X and O sites; and p_X , p_O are the values of the induced dipoles at these sites. These p values follow from solution of the equations

$$\begin{aligned} p_X(1 - \alpha_X K_1) - p_O(\alpha_X K_2) &= \alpha_X E_X, \\ -p_X(\alpha_O K_3) + p_O(1 - \alpha_O K_4) &= \alpha_O E_O, \end{aligned} \quad (2)$$

¹ A preliminary account was given by J. O. Artman and John C. Murphy in *Bull. Am. Phys. Soc.* **10**, 488 (1965).

² J. O. Artman and John C. Murphy, *Phys. Rev.* **135**, A1622 (1964).

TABLE I. Parameters computed from crystal geometry for a number of transition-metal sesquioxides. Crystal data as given in Ref. 3. Summations by cluster method were taken over spheres of radius $4A_0$. (Al_2O_3 entries are included for reference purposes.) As indicated in the text, these numerics are used in evaluation of the field gradient at the cation position. The results are in the cgs system. The appropriate power of 10 is indicated at the right-hand side of each line.

		Al_2O_3	Cr_2O_3	Fe_2O_3	Ti_2O_3	V_2O_3	
1.	q_m'	0.40424	0.30449	0.27247	0.81090	0.14911	$\times 10^{14}$
2.	q_{d-X}'	-0.08916	-0.10144	-0.05644	-0.12196	-0.09364	$\times 10^{32}$
3.	q_{d-O}'	-0.48672	-0.38704	-0.43792	-0.26120	-0.31460	$\times 10^{32}$
4.	E_X	0.27238	0.26412	0.04269	0.65924	0.55888	$\times 10^6$
5.	E_O	0.25751	0.64805	-0.03664	0.86393	0.64249	$\times 10^6$
6.	K_1	0.10012	0.07905	0.08986	0.05069	0.08764	$\times 10^{24}$
7.	K_2	-0.80877	-0.73529	-0.68075	-0.65537	-0.69506	$\times 10^{24}$
8.	K_3	-0.53913	-0.49020	-0.45384	-0.43691	-0.46337	$\times 10^{24}$
9.	K_4	-0.04313	-0.03937	-0.05191	-0.00103	-0.02528	$\times 10^{24}$

where the E 's denote the monopolar contributions to the electric field, the K 's designate appropriate factors necessary to specify the dipolar field contributions, and the α 's are the polarizabilities.

In order to make subsequent numerical manipulations transparent, we present for these sesquioxides a listing, in Table I, of the numerics computed from crystal geometry. The lattice parameters of Newnham and de Haan³ were employed. We use the cgs system. Accordingly, q_m' is expressed in units of 10^{14} , q_{d-X}' and q_{d-O}' in units of 10^{32} , the E 's in units of 10^6 and the K 's in units of 10^{24} . For comparison purposes we include our previous tabulation² of Al_2O_4 parameters.

The numerical values listed were obtained from lattice summations within spheres of $4A_0$ in radius. The "cluster" method was employed. The advantage of this procedure over conventional methods had been discussed previously.² It is demonstrated in Table II for the case of E_O in $\alpha-Al_2O_3$.

In addition to these geometrically dependent terms, the evaluation of q' requires the selection of appropriate

α 's. Previously we had concluded² that the analysis of Tessman *et al.*,⁴ which involved a simple application of the Clausius-Mossotti formula, was appropriate in this respect. Furthermore, since the cation polarizability in these sesquioxides is expected to be relatively small, virtually all the polarizability would be assigned to the oxygen ions.

In the interval between the preparation of our two papers, articles by Ruffa⁵ and Taylor and Das⁶ have appeared which relate to the specification of polarizability. Ruffa contends that the cation polarizability in crystal lattices could be enhanced significantly over the free-ion value. His procedure involves estimating the polarizability through determination of the ionic radius *in situ*, obtained, for example, from examination of an electron-density map. In TiO_2 Ruffa⁵ by this method found a ten-fold increase in the polarizability of the Ti^{4+} ion. The only data applicable to these sesquioxides that we have been able to locate are depicted in Fig. 4 of Abrahams'⁷ paper on Ti_2O_3 . The extension of the Ti^{3+} ion is 0.34 \AA which leads to an insignificant α_{Ti} value. We will assume that the situation in the other sesquioxides is much the same. Thus, regardless of the general validity of Ruffa's argument, we feel that cation polarizability enhancement is unimportant in these sesquioxides.

In their study of BeO , Taylor and Das⁶ draw a distinction between several different dipolar polarizabilities. In their notation these include the optical frequency polarizability for the free ion (α') and for the ion bound in a lattice (α''), the apparent polarizability in the local crystalline field (α), and the incremental polarizability with respect to additional local static field ($\bar{\alpha}$). Taylor and Das prefer to evaluate α from α'' and $\bar{\alpha}$, obtaining 2.19 \AA^3 for O^{2-} in BeO . (They assert that the Be^{2+} polarizability contribution is not significant.)

As we will discuss later in more detail, Sharma and Das⁸ have also evaluated field gradients for a number

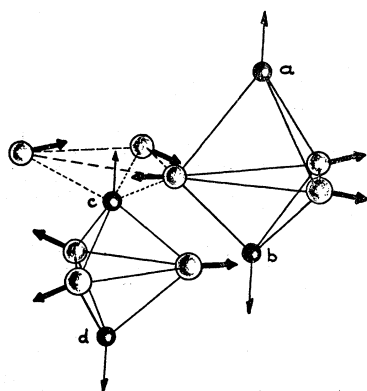


FIG. 1. Two of the bipyramids of the corundum-type lattice. In all cases considered, *except* Fe_2O_3 , the electric dipoles borne by the O^{2-} ions (large white spheres) are directed *outwardly* from the centers of the equilateral triangles to which they pertain. The cation and oxygen dipoles are defined in the *positive* sense when directed as shown in this figure. The electric field gradient at cation positions (small black spheres) then is composed of a positive monopolar contribution and a negative O^{2-} dipolar contribution.

³ R. E. Newnham and Y. M. de Haan, *Z. Krist.*, **117**, 235 (1962).

⁴ J. R. Tessman, A. H. Kahn, and W. Shockley, *Phys. Rev.* **92**, 890 (1953).

⁵ A. R. Ruffa, *Phys. Rev.* **133**, A1418 (1964); **130**, 1412 (1963).

⁶ T. T. Taylor and T. P. Das, *Phys. Rev.* **133**, A1327 (1964).

⁷ S. C. Abrahams, *Phys. Rev.* **130**, 2230 (1963).

⁸ R. R. Sharma and T. P. Das, *J. Chem. Phys.* **41**, 3581 (1964).

of sesquioxides. Since no $\tilde{\alpha}$ data for the sesquioxides seem to be available they used the BeO value for this purpose. In view of possible questions concerning the validity of applying an α value derived for one lattice to other lattices of different structure, we believe that a simple application of the Clausius-Mossotti relation, neglecting cation α , is a reasonable procedure at the present time. (An inspection of the data shows that the numerical differences in q' arising from these different α_0 selections are not particularly significant, except for Al_2O_3 . Here Sharma and Das¹⁸ value of q' is about one-half ours.²)

In order to evaluate α_0 from index of refraction data we will require the "molecular" unit volumes $A_0^3 C_0 / (4\sqrt{3})$ which, for the Al, Cr, Fe, Ti, and V sesquioxides, are (in \AA^3): 42.46, 48.30, 50.30, 52.20, and 49.56, respectively. If we then simplify Eqs. (1) and (2) by setting $\alpha_X \simeq 0$ we find that

$$p_0 \simeq \alpha_0 E_0 / (1 - \alpha_0 K_4)$$

and

$$q_X' \simeq q_m' = q_{a-o'} \alpha_0 E_0 / (1 - \alpha_0 K_4). \quad (3)$$

The Table I entries of immediate concern are those of q_m' , $q_{a-o'}$, E_0 , and K_4 . However, if later it is desirable to refine the analysis by including cation polarizability the complete entries of Table I are available. We note that the q' 's and some of the K 's correspond to summations which are comparatively insensitive to small changes in geometry. That is, for a parameter f , the logarithmic variation $|\Delta f/f|$ is less than or of the order of magnitude of unity when comparing the various sesquioxides. For example, q_m' ranges from 0.15 to 0.40 while $q_{a-o'}$ extends from -0.26 to -0.49 . On the other hand, K_4 is more sensitive to geometry. Its value covers the range -0.001 to -0.052 ($\times 10^{24}$) with a maximum $|\Delta f/f| > 50$. Fortunately, since α_0 is of the order 2×10^{-24} , it is clear that the $\alpha_0 K_4$ reaction term in the denominators above will not be very significant.

For all cases except Fe_2O_3 E_0 is positive, ranging from 0.26 to 0.65 in value. Hence from Eqs. (3) and Table I we find that in these lattices the monopolar and dipolar contributions to the field gradient q_X' are of opposite sign and, it turns out, comparable in magnitude. In Fe_2O_3 , on the other hand, the dipolar and monopolar contributions are positive. In this case the dipolar contribution to the field gradient is much the smaller. Detailed numerical evaluations for the various crystals follow.

COMPUTATIONS OF q' AND Q

Cr⁵³

The absolute value of the quadrupole coupling constant, $eQ(1-\gamma_\infty)q'$ recently has been found from low-temperature NMR observations⁹ to correspond to

⁹ M. Rubinstein, G. H. Stauss, and J. J. Krebs, Phys. Letters 12, 302 (1964).

TABLE II. Comparison of the conventional and cluster methods for computing the monopolar electric field at an oxygen site (E_0). R denotes the radius of the sphere which envelops the ions (or cluster centroids). The tabulations refer to α - Al_2O_3 . The particular oxygen site is such that the electric field should be directed at an angle (α) of 120° . The E_0 value at $4A_0$ radius is entered in Table I.

R/A_0	Conventional method		Cluster method	
	E_0	α (degrees)	E_0	α (degrees)
1	0.33454	120.0
2	0.23565	-63.7	0.27474	120.0
3	0.08321	-24.4	0.25715	119.9
4	0.18493	113.8	0.25751	119.9
5	0.25838	120.0
6	0.25835	120.0

$|0.525| \pm 0.020$ Mc/sec. The Sternheimer factor, $1 - \gamma_\infty$, is 10.8.¹⁰ The index of refraction for Cr_2O_3 is 2.5. From the Clausius-Mossotti relation we find that α_0 equals 2.44×10^{-24} . On this basis $q' \times 10^{-14} \simeq 0.304 - 0.558 = -0.254$. We note here that the dipole contribution toward the field gradient is approximately twice the monopolar contribution, reversing the algebraic sign. Our final value for $|Q|$ of Cr^{53} is 0.026 b. In its absolute sense this is within the range of our earlier estimates² from ruby data: $+0.02 \leftrightarrow +0.05$ b.

Fe^{57m}

The quadrupole interaction has been studied extensively by Mössbauer techniques. Ono and Ito, for example,¹¹ report a quadrupole coupling constant at 260°K of $+9.7 \pm 0.9$ Mc/sec. Within experimental error this agrees with earlier results such as those of Wertheim and Buchanan.¹² The Sternheimer factor is 10.14.¹³ The Fe_2O_3 index of refraction is 3.0 which corresponds to an $\alpha_0 \sim 2.91$. We find $q' \times 10^{-14} \simeq 0.272 + 0.041 = 0.313$. Hence $Q = +0.41$ b. (Neglect of the dipole term corresponds to a resultant Q of $+0.49$ b.) The Q value obtained by Ingalls from ferrous compound studies¹⁴ is $+0.29 \pm 0.02$ b. (This represents an upward scaling from his earlier estimate¹⁵ of $+0.15$ b.) Contrary to assertions in the literature,^{8,14} it does not seem possible to reconcile the Q obtained from ferrous compounds with the interpretations from α - Fe_2O_3 data.

Ti^{47,49}

The titanium isotopes 47 and 49 bear nuclear spins of $\frac{5}{2}$ and $\frac{7}{2}$, respectively. However, we have not been able to find any pertinent Ti_2O_3 quadrupole data. Extrapolating from the Cr and Fe sesquioxides we

¹⁰ R. M. Sternheimer, quoted as private communication by N. Laurance and J. Lambe, Phys. Rev. 132, 1029 (1963).

¹¹ K. Ono and A. Ito, J. Phys. Soc. Japan 17, 1012 (1962).

¹² G. K. Wertheim and D. N. E. Buchanan, in *Proceedings of the Second International Conference on the Mössbauer Effect, Saclay, France, 1962* (John Wiley & Sons, Inc., New York, 1962), p. 130.

¹³ R. M. Sternheimer, Phys. Rev. 130, 1423 (1963).

¹⁴ R. Ingalls, Phys. Rev. 133, A787 (1964).

¹⁵ R. Ingalls, Phys. Rev. 128, 1155 (1962).

TABLE III. Quadrupole and related data for the trivalent cations of a number of transition-metal sesquioxides. Entries for Al²⁷ are included for reference purposes.

Nucleus	Al ²⁷	Cr ⁵³	Fe ^{57m}	Ti ^{47,49}	V ⁵¹
$eQ(1-\gamma_\infty)q'$ (Mc/sec)	2.40 ^a	0.525 ^b	9.7 ^c	...	6.4 ^d
$1-\gamma_\infty$	3.59 ^e	10.8 ^f	10.14 ^g	~11 ^h	~11 ^h
$10^{-14}q'$ (esu) ⁱ	0.245	-0.254	0.313	≈0.27	~0.31
Q (barn) ⁱ	0.377	0.026	0.41	...	0.26
Q (barn)	0.149 ^j	0.02 to 0.05 ^k	0.29 ^l	0.35, 0.4 ^m	0.3 ⁿ 0.0073 ^o

^a Reference 21.

^b Reference 9.

^c Reference 11.

^d Reference 17.

^e Reference 22.

^f Reference 10.

^g Reference 13.

^h Our estimate, extrapolation from Cr³⁺ and Fe³⁺.

ⁱ Computed in this paper.

^j Reference 23.

^k Reference 2.

^l Reference 14.

^m Reference 16.

ⁿ Reference 18.

^o Reference 20.

estimate $1-\gamma_\infty$ to be about 11 and α_0 to be roughly 2.4. We find then that $q' \times 10^{-14} \sim 0.81 - 0.54 = 0.27$ (close to the net Fe₂O₃ value) but are unable to proceed further. Weber and Allen,¹⁶ from research on SrTiO₃, estimated the Q values of Ti^{47,49} to be 0.35 and 0.4 b, respectively.

V⁵¹

Jones has estimated from NMR¹⁷ that $|eQ(1-\gamma_\infty)q'|$ is ~ 6.4 Mc/sec. As in the Ti case, we estimate $1-\gamma_\infty$ and α_0 to be 11 and 2.4, respectively. We find that $q' \times 10^{-14} \sim 0.15 - 0.46 = -0.31$, close to the Cr₂O₃ value; $|Q|$ then is 0.26 b. This is in good agreement with the value of 0.3 b deduced from optical spectroscopy.¹⁸ However, recent NMR studies^{19,20} have suggested a much smaller value. Nagasawa and coworkers²⁰ from a study of V₂O₅ conclude that $|Q|$ is 0.0073 b. However, in view of the neglect of oxygen polarization and of the nature of the Sternheimer factor estimation, it is hard to assess the validity of this result.

Al²⁷

We repeat here our previous² corundum calculation. $eQ(1-\gamma_\infty)q'$ is²¹ $+2.40$ Mc/sec. Using an α_0 of 1.34 (Ref. 2) we find $q' \times 10^{-14} = 0.404 - 0.159 = 0.245$, close to the Fe₂O₃ and Ti₂O₃ lattice results. Applying Das and Bersohn's calculation²² of $1-\gamma_\infty$ (3.59) we find Q to be 0.377 b. This is twice the value found by independent techniques.²³ The implications of this discrepancy have been the subject of some discussion.^{2,8,24}

CRITIQUE OF RELATED COMPUTATIONS

Sharma and Das recently have also reported⁸ on q' and Q calculations in Al₂O₃, Cr₂O₃, and Fe₂O₃, using

¹⁶ M. J. Weber and R. R. Allen, J. Chem. Phys. **38**, 726 (1963).

¹⁷ E. D. Jones, Bull. Am. Phys. Soc. **9**, 24 (1964).

¹⁸ K. Murakawa and T. Kamei, Phys. Rev. **92**, 325 (1953).

¹⁹ R. G. Barnes and T. P. Graham, Phys. Rev. Letters **8**, 248 (1962).

²⁰ H. Nagasawa, S. K. Takeshita, and Y. Tomono, J. Phys. Soc. Japan **19**, 764 (1964).

²¹ R. V. Pound, Phys. Rev. **79**, 689 (1950).

²² T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956).

²³ H. Lew and G. Wessel, Phys. Rev. **90**, 1 (1953).

²⁴ N. Laurance, E. C. McIrvine, and J. Lambe, J. Phys. Chem. Solids **23**, 515 (1962).

relations equivalent to our Eqs. (3). Various differences between these calculations and ours exist. Some are due simply to the choice of α_0 ; these investigators preferred the Taylor and Das⁶ BeO value of α , 2.19 Å³. However, the more significant discrepancies arise in the evaluation of the geometrically dependent quantities.

Sharma and Das designate the parameters which correspond to our K_4 and E_0 by E_a/μ and E_m , respectively. In turn E_a/μ is proportional to ζ and E_m to $3\xi - 2\eta$ (ξ being the cation contribution and η the anion contribution). Table II of Ref. 8 contains tabulations of ξ , η , and ζ . (The quantity equivalent to $q_{d-o'}$ unfortunately is not explicitly tabulated.) Upon making the appropriate conversions from the entries in this table we find K_4 values of 0.06628, 0.05693, and 0.05126, respectively, for the Al, Cr, and Fe sesquioxides. Similarly we find E_0 values of -0.26328 , -0.54692 , and $+0.12653$, respectively. Upon comparison with the corresponding entries in our Table I we note that the magnitudes differ by amounts which we believe cannot be attributed to a slightly different selection of crystal lattice parameters. (See particularly the case of the Fe₂O₃ E_0 value for which we obtained -0.03664 . We have recomputed E_0 , using the Fe₂O₃ parameters employed by Sharma and Das, obtaining a value 5% greater than our Table I entry. Obviously such slight variations in input parameters cannot account for the discrepancy.) Although the disagreement in the K_4 's is of technical interest, its practical import fortunately is minimized in view of the numerically small value of the $\alpha_0 K_4$ reaction term.

We also find that all the algebraic signs are reversed. In the case of the E_0 's at least, a compensatory sign change may have been made elsewhere by Sharma and Das, since they have the dipoles directed in the proper sense. In general we believe that, where discrepancies occur between our results and those of Sharma and Das, the cluster type of calculation is to be preferred.

APPLICATIONS TO Fe^{57m}

The computational differences are particularly significant in the case of Fe₂O₃. Ingalls¹⁴ concluded from his analysis of Fe^{57m} quadrupole splitting in the *ferrous*

compound $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ that $Q = 0.29 \pm 0.02$ b. In this configuration (${}^5D, 3d^6$), the important contribution to the field gradient seen by the nucleus is associated with the charge distribution of the aspherical $3d$ "valence" electron. The gradient contribution arising from the disposition of the ions in the lattice is small. On the other hand, for Fe^{3+} only the lattice contribution would exist if it were actually in the ${}^6S_{5/2}, 3d^5$ configuration. The Fe^{57m} Mössbauer isomer shift has been used to evaluate the admixture of s character into the $3d^5$ state. An interpretation made for $\alpha\text{-Fe}_2\text{O}_3$ by Walker, Wertheim, and Jaccarino²⁵ leads to an admixture of about 2%. One might assume therefore that $\alpha\text{-Fe}_2\text{O}_3$ would be an ideal lattice in which to evaluate ferric quadrupole data.

The consensus as to the correspondence of the ferrous and ferric Q values had vacillated with revisions of theory and calculation.^{8,14,15} Sharma and Das,⁸ by virtue of their field-gradient computations, interpreted the Mössbauer observations of $(\text{Fe}^{57m})^{3+}$ in Fe_2O_3 to correspond to $+0.277$ b, in excellent agreement with Ingalls' result—thus apparently disposing of the ferrous-ferric anomaly. It is clear, however, from our analysis that this conclusion is not tenable, most of the difficulty arising in the over-evaluation of E_0 . It also would follow that the dipole contributions to the Fe^{3+} crystal field terms in $\alpha\text{-Fe}_2\text{O}_3$ numerically are much less significant than supposed by these authors. [In this connection we have prepared tabulations of the dipolar potential constants for the Cr, Fe, Ti, and V sesquioxides (see Tables VIII and IX of Ref. 2)²⁶ which are available upon request.]

CONCLUSIONS

We have presented an evaluation of the electric field gradient q' at the cation sites in the Cr, Fe, Ti, and V sesquioxide crystal structures isomorphous to corundum. We have included point dipole as well as point

monopole lattice sum contributions. In so far as existing nuclear quadrupole data permit, we have used these tabulations to determine the electric nuclear quadrupole moments (Q) of the appropriate odd isotopes.

Our intent has been to present a reliable compilation of the geometrically dependent parameters. (Unless contributions are properly grouped, many of the pertinent corundum lattice sums converge slowly.) We find, for all cases but $\alpha\text{-Fe}_2\text{O}_3$, that the dipolar field gradient contributions are opposite in sign to the monopolar and of the same order of magnitude. Thus the net algebraic sign of q' depends on the interplay of these two effects. Within our framework the final specification of q' then depends upon the choice of the polarizability assigned to the oxygen ions and cations. We have reviewed briefly the contentions of some recent papers on polarizability. In view of experimental and theoretical uncertainties, we felt it appropriate at this time to neglect cation polarization and simply specify the oxygen polarizability through the Clausius-Mossotti relation and optical refraction data. Nevertheless our tables have the data necessary when recomputing q' for other cation and oxygen polarizability choices.

The Q values deduced here seem to be somewhat larger than the results of other estimates. This seems to be the case for Al^{27} , Fe^{57m} , and probably V^{51} . Insufficient information is available on $\text{Ti}^{47,49}$. Previous data on Cr^{53} , taken on ruby, are not clear-cut in this respect.² In view of extensive Mössbauer spectroscopy, the Fe^{57m} result is of special interest. Chemically $\alpha\text{-Fe}_2\text{O}_3$ is simple in the sense that the admixture of s character into the $\text{Fe}^{3+} 3d^5$ state is no more than 2%. From our point of view it appears unique in that the dipolar q' contribution is in the same sense as the monopolar and comparatively small. (The specific value of α_0 thus is not an important consideration.) We find $Q(\text{Fe}^{57m})$ to be 0.41 b as compared to the value of 0.29 b deduced by Ingalls^{14,15,27} from experiments in the ferrous compound $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$. We believe that recent $\alpha\text{-Fe}_2\text{O}_3$ lattice summations, which corresponded to a $Q(\text{Fe}^{57m})$ of 0.277 b, are in error.

²⁵ L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters **6**, 98 (1961).

²⁶ The number preceding "p" in the equation for B_4^3 of Table IX of Ref. 2 should be 35 instead of 3. The corresponding computations of this reference, however, have been calculated properly.

²⁷ B. Höflinger and J. Voigtländer, Z. Naturforsch. **18a**, 1065 (1963); **18a**, 1074 (1963); **18a**, 1185 (1963), from a study of $\text{Fe}(\text{C}_6\text{H}_5)_2$, find $Q(\text{Fe}^{57m})$ to be 0.18 b.