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Nuclear Quadrupole Moment of ^{57m}Fe from α-Fe_2O_3 Data*

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The electric-field gradient at the Fe^{3+} site in hematite (α-Fe_2O_3) has been recomputed by use of the ionic model, including contributions of electronic dipole and quadrupole moments of the oxygen ion, as well as apparent quadrupolar effects due to thermal vibration of oxygen. The calculations have been performed self-consistently for various parameter sets of dipole and quadrupole polarizabilities, α_D and α_Q. As in corundum (α-Al_2O_3), the field gradient is insensitive to α_D because of the (accidentally) nearly vanishing field at the oxygen position. α_Q, however, is a sensitive parameter. The vibrational contribution is small, being $\sim5\%$ of the total field gradient. Assuming a dipole polarizability $\alpha_D(O^{2-})=2.91$ Å^3, we find a range of values for the nuclear quadrupole moment of the 14.4-keV excited state of ^{57m}Fe, depending on $\alpha_Q(O^{2-})$, which is not well known. For $\alpha_Q(O^{2-})=0$, $Q(^{57m}\mathrm{Fe})=0.29$ b. For $\alpha_Q=0.3$, $Q=0.16$ b.

INTRODUCTION

A NUMBER of attempts have been made to determine the nuclear electric quadrupole moment Q of the 14.4-keV excited state of ^{57m}Fe from nuclear quadrupole coupling constants e^2qQ obtained from Mössbauer-effect spectroscopy.[1-7] One of the typical approaches has been to use simple, predominantly ionic crystal structures, such as α-Fe_2O_3 (hematite), and to calculate the electric-field gradient at the Fe^{3+} site by summation over point-charge or point-dipole lattices. The difficulty with this approach is that the point multipole expansion converges slowly, especially if it is used for the computation of ionic-potential derivatives at cationic sites in oxidic crystals. The reason is the critical dependence of the derivatives on the unknown ionic polarizabilities of oxygen. α-Fe_2O_3 is a good example of the inadequacy of the simple point-dipole approach.

In this article, self-consistent electric-field gradients at the Fe^{3+} site in hematite are calculated by use of the ionic model, including dipole and quadrupole moments of the oxygen ion. The calculations have been performed for various sets of polarizabilities to illustrate the dependence on these parameters. A full description of the calculation, including notation and units, may be found in a report by Hafner and Raymond[8] on corundum (α-Al_2O_3), which is isomorphous to hematite.

A discrepancy in the value of Q based on data for ferric versus ferrous compounds has been noted.[1] We investigate here the effect of including induced quadrupole moments on this discrepancy.

SELF-CONSISTENT IONIC-POTENTIAL DERIVATIVES AT LATTICE SITES

Crystal fields in hematite are best described in the rhombohedral system which can be transformed to a rectangular system with three equivalent axes without loss of symmetry (cf. Table I). In this system, the ionic potentials and their first and second derivatives at the Fe^{3+} and O^{2-} sites in hematite are completely determined by eight potential components V_i, which are related to each other by the equations

$$V_i=V_i{}^M+\sum_{j=3}^{8} K_{ij}\alpha_j V_j. \tag{1}$$

V_1 and V_2 are the Madelung potentials, $\sqrt{3}V_3=V_r(Fe^{3+})$, and $\sqrt{2}V_5=V_S(O^{2-})$ are the potential gradients at Fe^{3+} and O^{2-} sites, respectively. $V_4=V_{rr}(Fe^{3+})$ is the second derivative (negative field gradient) at Fe^{3+} parallel to the trigonal axis. V_6, V_7, and V_8 are the second derivatives (negative field-gradient components) V_{xx}, V_{xy}, and V_{xz} at the oxygen sites. The dipole polarizability of $Fe^{3+}(-\alpha_3)$ and the quadrupole polarizability of $Fe^{3+}(-\alpha_4)$ are assumed to be negligible.[9] $-\alpha_5=\alpha_D$, and $-\alpha_6=-\alpha_7=-\alpha_8=\alpha_Q$, respectively, represent the dipole and quadrupole polarizabilities of O^{2-}. For more details about the notation the reader is referred to Ref. 8. The monopole terms $V_i{}^M$ and the crystallographic K_{ij} factors have to be found by lattice summation. For this the Ewald-

TABLE I. Transformation matrix rhombohedral (a_r,α_r)–rectangular(x,y,z).

	$a\ \ b\ \ b$		$a=5.01994$	
	$b\ \ a\ \ b$		$b=1.45985$	
	$b\ \ b\ \ a$			
Fe	u,u,u; etc.	$u=0.10528$ [a]	$a_h=5.0346$ Å	$a_r=5.4279$ Å
O	$v,-v,0$; etc.	$v=0.3072$ [a]	$c_h=13.752$ Å	$\alpha_r=55°16'$

[a] Blake, Finger, and Zoltai (Ref. 10).

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[1] J. O. Artman, A. H. Muir, Jr., and H. Wiedersich, Phys. Rev. **173**, 337 (1968).

[2] C. B. Harris, J. Chem. Phys. **49**, 1648 (1968).

[3] A. J. Nozik and M. Kaplan, Phys. Rev. **159**, 273 (1967).

[4] C. E. Johnson, Proc. Phys. Soc. (London) **92**, 748 (1967).

[5] F. S. Ham, Phys. Rev. **160**, 328 (1967).

[6] M. Weissbluth and J. E. Maling, J. Chem. Phys. **47**, 4166 (1967).

[7] F. van der Woude and A. J. Dekker, Phys. Status Solidi **13**, 181 (1966).

[8] S. S. Hafner and M. Raymond, J. Chem. Phys. **49**, 3570 (1968).

[9] The potential gradient $V_r{}^M$ at the Fe^{3+} site due to the point charges is 0.2712×10^6 esu. The dipole polarizability α of Fe^{3+} is unknown. Assuming $\alpha(Fe^{3+})=0.1$ Å^3 and using K_{35} (Table II) we find a value of 0.0217×10^{14} esu as contribution to the field gradient $V_{rr}(Fe^{3+})$.

TABLE II. Crystallographic K_{ij} factors of hematite (cgs units).[a]

$j \backslash i$	3	4	5	6	7	8
3	-0.0766×10^{24}		$+0.5402\times10^{24}$			
4						
5	$+0.5402\times10^{24}$	-0.2811×10^{32}	$+0.1277\times10^{24}$	$+0.0098\times10^{32}$	$+0.3583\times10^{32}$	-0.1323×10^{32}
6		$+0.4434\times10^{40}$	$+0.0074\times10^{32}$	$+0.0424\times10^{40}$	$+0.0316\times10^{40}$	-0.0715×10^{40}
7		-0.1304×10^{40}	$+0.0895\times10^{32}$	$+0.0105\times10^{40}$	$+0.0639\times10^{40}$	-0.0011×10^{40}
8		-0.2977×10^{40}	-0.0661×10^{32}	-0.0477×10^{40}	-0.0023×10^{40}	$+0.0368\times10^{40}$

[a] Definitions cf. Hafner and Raymond (Ref. 8).

potential sums were expanded in spherical harmonics. The summation was performed by use of the structural parameters of Blake, Finger, and Zoltai[10] (Table I). Summations over about 1500 ions were found to be sufficient for obtaining four significant figures for the V_i^M terms. The K_{ij} factors were obtained by the point-charge cluster technique. It should be noted that the K_{ij}'s are purely geometrical factors, and it is irrelevant whether the multipoles are of an ionic or nonionic nature. The factors are given in Table II. They can be compared with the previously reported values in Table III. They are rather similar to those of corundum, α-Al_2O_3 (Table III of Ref. 8). In contrast to the monopole terms they are not very sensitive to slight changes of atomic coordinates.[8]

RESULTS AND DISCUSSION

The ionic-field gradient at the Fe^{3+} position can be calculated for any combination of polarizability parameters by use of V_i^M, K_{ij}, and solution of the system of partially simultaneous equations (1). As with corundum, the polarizabilities are not well known. In the previous calculations, the dipole polarizability $\alpha_D = 2.91$ Å^3, derived from the index of refraction by the Clausius-Mossotti relation, was generally used. Here, we have calculated the field gradient for this polarizability, and for $\alpha_D = 2.0$ Å^3, as well as a number of different quadrupole polarizabilities α_Q. The total field gradient is plotted in Fig. 1 as a function of α_Q for both α_D values. It is evident that the field gradient is *not* sensitive to α_D, whereas it depends *critically* on α_Q. This is due to the fact that the electrostatic field at the oxygen position is accidentally small, while the field gradient at this position is large. With the quadrupole coupling constant[1] $e^2qQ = +0.880$ mm/sec and the antishielding factor[11] $\gamma_\infty = -9.14$, we find the quadrupole moments given in Table IV. The ionic multipole moments and the various contributions to the field gradient of Fe^{3+} are given in Table V. Thus, we find that a determination of Q by lattice-summation methods in Fe_2O_3 is possible only if $\alpha_Q(O^{2-})$ is accurately known. This fact has not been sufficiently recognized in previous work on this problem and therefore inadequate conclusions have been reached.

A few theoretical calculations of α_Q have been performed, using Hartree-Fock wave functions. The values obtained are 400–1000 Å^5.[12,13] Using contracted

TABLE III. Comparison with previous data of point-charge potential components and K factors.

Notation[a]	Units	This work	AMW[b]
V_r^M(Fe)	10^6 esu	-0.27120	-0.27469
V_s^M(O)	10^6 esu	0.06228	0.06589
V_{rr}^M(Fe)	10^{14} esu	0.4261	0.42422
V_{xx}^M(O)	10^{14} esu	-1.3643	
V_{xy}^M(O)	10^{14} esu	-1.8006	
V_{xz}^M(O)	10^{14} esu	0.4879	
$K_1 = -K_{33}$	10^{24} cm^{-3}	0.0766	0.09032
K_2[c,d] $= -(\sqrt{3}/\sqrt{2})K_{35}$	10^{24} cm^{-3}	-0.6616	-0.66161[d]
K_4[e] $= -K_{55}$	10^{24} cm^{-3}	-0.1277	-0.03358[e]
eq_{d-0}[c]	10^{32} esu	-0.3975	-0.39736

[a] Reference 8.
[b] Reference 1.
[c] Notation of Ref. 1.
[d] K_{35} is equal to K_{53} due to symmetry. Therefore $K_3 = \frac{2}{3}K_2$ in Artman *et al.*
[e] This inconsistency also exists in J. O. Artman and J. C. Murphy, Phys. Rev. **135**, 1622 (1966) and in J. O. Artman, *ibid.* **143**, 541 (1966).

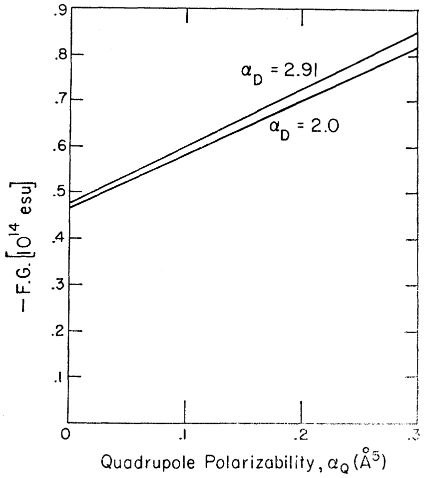

FIG. 1. Dependence of second derivative of the potential (negative electric-field gradient) at Fe^{3+} site in hematite on quadrupole polarizability of the oxygen ion.

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[10] We are grateful to Dr. R. L. Blake for providing us with the data prior to publication; coordinates and lattice constants are also quoted in Ref. 1.

[11] R. M. Sternheimer, Phys. Rev. **130**, 1423 (1963).

[12] P. W. Langhoff and R. P. Hurst, Phys. Rev. **139**, A1415 (1965).

[13] J. Lahiri and A. Mukherji, Phys. Rev. **153**, 386 (1967).

TABLE IV. Quadrupole moment of ^{57m}Fe for various oxygen-ion polarizabilities.

α_D (Å^3)	α_Q (Å^5)	$-$F.G.$=V_{rr}$(Fe^{3+}) ($\times 10^{14}$ esu)	$Q(^{57m}\mathrm{Fe})$ [a] (b)
2.0	0	0.4655	+0.299
2.0	0.10	0.5858	0.237
2.0	0.20	0.7036	0.197
2.0	0.30	0.8189	0.170
2.0	0.50	1.0426	0.133
2.91	0	0.4786	0.290
2.91	0.10	0.6051	0.230
2.91	0.20	0.7292	0.191
2.91	0.30	0.8508	0.163
2.91	0.50	1.0920	0.127

[a] Using γ_∞ (Fe^{3+}) $= -9.14$.

wave functions, Burns and Wikner[14] calculated 7 Å^5. All these values are much too large. For instance, if we use $\alpha_Q = 5$ Å^5 in our calculation, we find $Q = 0.03$ b. Lattice-sum calculations in corundum,[8] using a variable parameter approach, indicate an α_Q of about 0.2 Å^5. Similar calculations in kyanite (triclinic Al_2SiO_5) [15] reckon $\alpha_Q(O^{2-})$ to be about 0.1 Å^5. The polarizability of course depends on the crystal structure, so the range of values 0–0.5 Å^5 was chosen for this calculation. Without more definite information on this polarizability however, the $Q(^{57m}\mathrm{Fe})$ remains quite uncertain.

It is to be noted that in corundum-type structures, the quadrupolar contribution to the field gradient at the cationic site appears to be larger than the dipolar contribution. This is due to the fact that the field at the oxygen site is (accidentally) nearly zero. It is slightly positive in corundum and slightly negative in hematite. The field gradient at O^{2-}, however, is large. In crystal structures with more general point symmetries at the ionic sites (e.g., kyanite) the quadrupolar effects are found to be considerably smaller than the dipolar effects.

TABLE V. O^{2-} multipole moments and Fe^{3+} field gradients in hematite ($\alpha_D = 2.91$ Å^3; $\alpha_Q = 0.1$ Å^5).

		esu
O^{2-}	Dipole moment	-0.1942×10^{-18}
O^{2-}	Quadrupole moment[a,b]	
	Q_{xx}	$+0.1354\times 10^{-26}$
	Q_{xy}	$+0.1834\times 10^{-26}$
	Q_{xz}	-0.0494×10^{-26}
Fe^{3+}	Field gradient (second derivative of the potential)[b]	
	Point charge	$+0.4261\times 10^{14}$ esu
	Dipole	$+0.0772\times 10^{14}$ esu
	Quadrupole	$+0.1018\times 10^{14}$ esu
	Total	$+0.6051\times 10^{14}$ esu

[a] x, y, z according to Table I.
[b] Static contribution only.

TABLE VI. Thermal and electrostatically-induced quadrupole moments of the oxygen ion in α-Fe_2O_3.

[a]	Thermal natural[b] 10^{-26} esu	Thermal synthetic[c] 10^{-26} esu	Electrostatic $\alpha_D = 2.91$ Å^3; $\alpha_Q = 0.1$ Å^5 10^{-26} esu
Q_{xx}	+0.012	+0.008	+0.135
Q_{xy}	+0.019	+0.038	+0.183
Q_{xz}	−0.044	−0.021	−0.049
Q_{yy}	+0.012	+0.008	+0.135
Q_{yz}	−0.044	−0.021	−0.049
Q_{zz}	−0.024	−0.016	−0.271

[a] x, y, z system according to Table I.
[b] Reference 16.
[c] Reference 10; the temperature coefficients of oxygen are (in units of 10^3) $\beta_{11} = 2.7$, $\beta_{22} = 5.4$, $\beta_{33} = 0.2$, $\beta_{12} = 2.7$, $\beta_{13} = 0.25$, $\beta_{23} = 0.5$. For dimensions cf. Ref. 16.

The anisotropic temperature coefficients given by Blake *et al.*[10,16] were used to calculate the thermal quadrupole moments at the oxygen site. The vibrational amplitudes were derived according to the formulation of Cruickshank.[17] The thermal quadrupole moment is defined as $Q_{ij} = 2e\langle u_{ij}^2\rangle$, where $\langle u_{ij}^2\rangle$ is the mean square amplitude of the thermal ellipsoid,[16] and e is the charge on the ion. The resulting moments are given in Table VI, with induced quadrupole moments given for comparison. The field gradient at the Fe^{3+} site due to thermal quadrupoles is $+0.033\times 10^{14}$ esu for natural hematite and 0.0097×10^{14} esu for synthetic α-Fe_2O_3. The thermal vibrations of the oxygen ion at room temperature contribute 2–5% to the field gradient at Fe^{3+}. This result is principally in agreement with that of Schwarzenbach[18] who considered vibrational contributions to the field gradient at the Al^{3+} position in $AlPO_4$.

It has been pointed out[1] that there is a disagreement between values of Q (^{57m}Fe) obtained from ferric- and ferrous-compound data. Most recent calculations based on ferrous-compound data indicate a Q (^{57m}Fe) of about 0.2 b.[3–5] Determinations of Q by other methods also result in Q of $\sim$0.2 b.[2,6] Van der Woude and Dekker calculated $Q = +0.28$ b in α-FeOOH (ferric),[7] but they used only the monopole contribution. We have found that the Q cannot be precisely determined in Fe_2O_3. Including the uncertainty due to the ionic polarization of O^{2-}, and neglecting covalency, Q varies between 0.29 and 0.16 b.

It would be interesting to perform similar calculations for other ferric compounds. Of course, covalent participation in the predominantly ionic Fe^{3+}—O^{2-} bonds will affect the external field gradient and Sternheimer factor at the Fe^{3+} site. But as long as the predominant, ionic contribution is still uncertain, due to insufficiently known O^{2-} polarizabilities, estimates of covalent contributions are an involved problem.

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[14] G. Burns and E. G. Wikner, Phys. Rev. **121**, 155 (1961).

[15] M. Raymond, Ph.D. thesis, submitted to the University of Chicago (unpublished).

[16] R. L. Blake, R. E. Hessevick, T. Zoltzi, and L. W. Finger, Am. Mineralogist **51**, 123 (1966).

[17] D. W. J. Cruickshank, Acta Cryst. **9**, 747 (1956).

[18] D. Schwarzenbach, Z. Kristallogr. **123**, 422 (1966).