a g value considerably smaller than the first excited state, and if the exchange interaction is large enough to cause a crossing of the levels, a sharp magnetization curve such as that found in UI_3 would result. Another possible mechanism suggested by Blume is that the biquadratic exchange terms are not negligible. These models have been considered in detail by Erdos and Rudra, and the results will be presented in a subsequent publication.

ACKNOWLEDGMENTS

The authors gratefully acknowledge many useful discussions with Professor R. A. Kromhout, Professor P. Erdos, and Professor R. D. Spence. We also wish to express our appreciation to the Oak Ridge National Laboratory and Dr. L. D. Roberts for lending us the UI_3 samples. We thank E. D. Sanford for help with design and construction of the low-temperature apparatus.

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

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A new value for the nuclear quadrupole moment $Q(Fe^{57m})$ of the 14.4-keV level of Fe^{57} based on α-Fe_2O_3 data has been determined from a detailed series of Mössbauer-effect quadrupole-interaction measurements, x-ray structure-parameter studies, and lattice-sum calculations (including dipole moments). At room temperature, $e^2qQ=+0.880\pm0.024$ mm/sec. This, when combined with the principal component of the electric field gradient tensor at the iron-ion site ($+4.910\pm10^{13}$ esu), yields $Q(Fe^{57m})=+0.283\pm0.035$ b. The calculated field gradient is *very* sensitive to slight variations in the α-Fe_2O_3 structure parameters, particularly so for the iron special position parameter. A careful analysis has been made of the uncertainty in the quadrupole moment determination, although the effects of covalency and quadrupole (and higher-order) polarizability have not been included. It was also found that the thermal history of the samples can influence significantly the measured quadrupole coupling constant. The present result is compared to other quadrupole moment determinations.

I. INTRODUCTION

A RECENT determination of the nuclear quadrupole moment Q of Fe^{57m} by one of us (JOA[1]), derived from the calculated electric field gradient and quadrupole interaction in a *ferric* compound, gave a value $Q=+0.41$ b. This was in substantial disagreement with the earlier result of Ingalls,[2] $Q=+0.29\pm0.02$ b, determined from *ferrous* compound data. The JOA result was based on an elaborate lattice-sum calculation of the electric field gradient (EFG) at the Fe^{3+} ion site in α-Fe_2O_3, coupled with the corresponding e^2qQ value obtained by Ôno and Ito[3] from Mössbauer-effect (ME) spectroscopy. It disagreed also with previous quadrupole-moment evaluations from Fe^{3+} data by Sharma and Das[4] and Sternheimer[5] (+0.277 and +0.28 b, respectively) which, together with Ingalls' value, had led to a Q consensus of $\sim+0.3$ b.

In an attempt to resolve this discrepancy, it was shown[6] that although the e^2qQ observed in α-Fe_2O_3 by ME could vary significantly depending on sample thermal history, the disparate values of Q could not be reconciled on the basis of e^2qQ measurements alone. Since the EFG calculation was very sensitive to structural-parameter changes (the crystallographic data[7] used by JOA, for example, were taken at room temperature, while the Ôno and Ito e^2qQ value was taken at 260°K), we have thought it advisable to reexamine this matter in some detail, especially in view of a recently published[8] refinement of the α-Fe_2O_3 structural param-

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[1] J. O. Artman, Phys. Rev. **143**, 541 (1966), denoted as JOA in text.

[2] R. Ingalls, Phys. Rev. **133**, A787 (1964).

[3] K. Ôno and A. Ito, J. Phys. Soc. Japan **17**, 1012 (1962).

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

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

[6] A. H. Muir, Jr., and H. Wiedersich, Bull. Am. Phys. Soc. **11**, 770 (1966).

[7] R. E. Newnham and Y. M. de Haan, Z. Krist. **117**, 235 (1962). [Based on B. T. M. Willis and H. P. Rooksby, Proc. Phys. Soc. (London) **65B**, 950 (1952); and G. Shirane, S. J. Pickart, R. Nathans, and Y. Ishikawa, J. Phys. Chem. Solids **10**, 35 (1959).]

[8] R. L. Blake, R. E. Hessevick, T. Zoltai, and L. W. Finger, Am. Mineralogist **51**, 123 (1966), denoted as BHZF in text.

eters. The present work correlates EFG calculations and ME data with available structural information. Adopting the JOA method for calculating the EFG, our intent was to see whether a discrepancy in the value of Q based on data for ferric versus ferrous compounds did in fact now exist. Preliminary reports of the present work have been presented.[9,10]

During the completion of this work, additional determinations of Q from Fe^{2+} compound data appeared,[11–13] indicating $Q \approx +0.2$ b, adding additional importance to the need for a reevaluation based on Fe^{3+} compound data. Because of the vast amount of quadrupole-interaction data available from ME spectroscopy, a reliable value for the quadrupole moment for the 14.4-keV level of Fe^{57} is of considerable importance.

II. QUADRUPOLE INTERACTION

Although α-Fe_2O_3 had been examined often by ME spectroscopy,[14] we made an extensive series of new measurements to determine the quadrupole interaction in a number of different specimens. The spectrometer, a loudspeaker-multichannel analyzer system using a room-temperature Co^{57} in Pd source and a xenon-nitrogen proportional counter detector, was calibrated[15] with an iron foil at room temperature. The absorbers, "high-purity" materials from five different commercial suppliers and a number of synthetic single crystals[16] of α-Fe_2O_3, were given a variety of annealing treatments.

The EFG tensor for α-Fe_2O_3 is axially symmetric about the c axis. At room temperature the spin directions in this weak ferromagnet are normal to the c axis.[17] Consequently, for a quadrupole interaction small in comparison to the magnetic dipole interaction, the ME spectrum has hyperfine lines at positions given by[18]

$$\Delta E=\delta-(m_e g_e-m_g g_g)H+(-1)^{|m_e|+1/2}\epsilon', \qquad (1)$$

where δ is the isomer shift between source and absorber, $g_i=\mu_i/I_i$ is the nuclear gyromagnetic ratio for the level with spin I_i and nuclear magnetic moment μ_i, m_i is the nuclear magnetic quantum number, H is the internal magnetic field at the nucleus, and the subscripts g and e denote the ground and excited states, respectively. The displacement of the energy levels by the quadrupole interaction is given by[18]

$$\epsilon'=-\tfrac{1}{8}e^2qQ, \qquad (2)$$

where $-e$ is the charge of the electron and eq ($\equiv V_{zz}$) is the negative of the symmetry axis (z axis) component of the EFG tensor.

Below a temperature of ~260°K, α-Fe_2O_3 undergoes the Morin (spin-flip) transition in which the spins become aligned parallel and antiparallel to the c axis, for which case $\epsilon'=\epsilon=\frac{1}{4}e^2qQ$.

A nonlinear least-squares fitting of six Lorentzian line shapes was used to determine the line positions, from which the parameters δ, H, and ϵ' of Eq. (1) could be calculated by a linear (closed-form) least-squares analysis. The resulting expression for ϵ' is

$$\epsilon'=\tfrac{1}{8}[2(x_1+x_6)-(x_2+x_3+x_4+x_5)], \qquad (3)$$

where x_i denotes the position of the ith line.

Positive velocity corresponds to the source approaching the absorber. The room-temperature isomer shift ($+0.360\pm0.005$ mm/sec relative to metallic iron) and the internal magnetic field at the iron nucleus (516 ± 2 kOe) were the same for *all* samples within the uncertainty of the measurements. However, the quadrupole interaction ϵ' varied by more than 10% between the samples, depending on their thermal treatment.

Samples were given a variety of heat treatments to assess the effects of annealing, since in a number of x-ray and ME investigations of α-Fe_2O_3 samples annealed above 1000°C (presumably to remove imperfections) had been used. Figure 1 shows the room-temperature

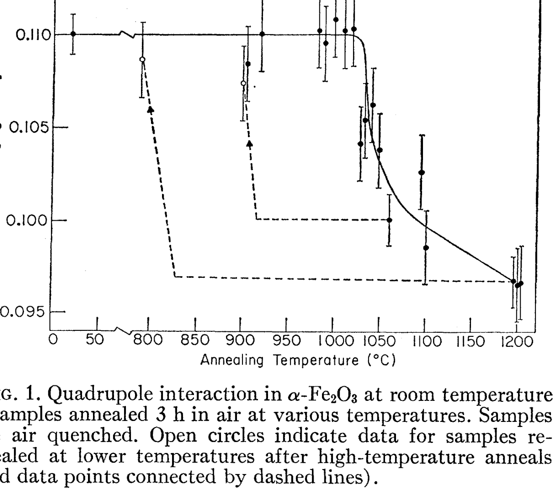

FIG. 1. Quadrupole interaction in α-Fe_2O_3 at room temperature for samples annealed 3 h in air at various temperatures. Samples were air quenched. Open circles indicate data for samples reannealed at lower temperatures after high-temperature anneals (solid data points connected by dashed lines).

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[9] A. H. Muir, Jr., H. Wiedersich, and J. O. Artman, in *Hyperfine Structures and Nuclear Radiations*, edited by E. Matthias and D. A. Shirley (North-Holland Publishing Co., Amsterdam, 1968), p. 236.

[10] J. O. Artman, A. H. Muir, Jr., and H. Wiedersich, Bull. Am. Phys. Soc. **13**, 46 (1968).

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

[12] C. E. Johnson, in *Hyperfine Structures and Nuclear Radiations* (North-Holland Publishing Co., Amsterdam, 1968), p. 226; Proc. Phys. Soc. (London) **92**, 748 (1967).

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

[14] A. H. Muir, Jr., K. J. Ando, and H. M. Coogan, *Mössbauer Effect Data Index 1958–1965* (Interscience Publishers, Inc., New York, 1966).

[15] R. S. Preston, S. S. Hanna, and J. Heberle, Phys. Rev. **128**, 2207 (1962).

[16] We thank G. P. Espinosa for providing the single-crystal specimens.

[17] C. G. Shull, W. A. Strauser, and E. O. Wollan, Phys. Rev. **83**, 333 (1951).

[18] For example, see G. K. Wertheim, *Mössbauer Effect: Principles and Applications* (Academic Press Inc., New York, 1964), Chap. VII. Equation (1) is valid under the condition $|\frac{1}{4}e^2qQ/g_eH|\ll1$. If the more general and exact formulation for this problem (e.g., p. 83) is expanded, it can be shown that the fractional correction to be applied in deriving ϵ' from Eq. (1) is $\frac{3}{8}(\frac{1}{4}e^2qQ/g_eH)^2$. For α-Fe_2O_3, neglecting this correction amounts to an error of ~0.14%, which is quite small in comparison with the accuracy of the measurement.

TABLE I. Recent structural parameters for α-Fe_2O_3.

Reference	Material	a_h [Å]	c_h [Å]	x (O)	z (Fe)
Blake *et al.*[a]	Synthetic	5.0346±0.0008	13.752±0.003	0.3072±0.0007	0.35528±0.00008
Blake *et al.*[b]	Natural	5.038 ±0.002	13.772±0.012	0.3059±0.001[c]	0.3553 ±0.0001[c]
Nordmark[d]	Synthetic	···	···	0.306 ±0.006	0.3548 ±0.0010
Cox *et al.*[e]	Synthetic	5.034	13.745	0.302 ±0.003	0.355 ±0.002
Newnham and de Haan[f]	Natural	5.0345	13.749	···	···
	Synthetic	···	···	0.300	0.355

[a] Reference 21 (BFZ).

[b] Reference 8 (BHZF).

[c] The reevaluated standard deviations are from Ref. 21, and are a factor of 10 larger than the standard deviations originally given in Ref. 8.

[d] Reference 19.

[e] D. E. Cox, W. J. Takei, and G. Shirane, J. Phys. Chem. Solids 24, 405 (1963).

[f] Reference 7.

results of one series of annealing experiments. Samples from one of the batches of commercial material were given 3-h annealing treatments in air, followed by air quenches. As indicated by the dashed lines, the apparent decrease in ϵ' is reversible upon reannealing at lower temperature. The flux-grown synthetic single-crystal specimens also exhibited an abnormally low value of ϵ' as initially grown. However, measurements after annealing at modest temperatures (<1000°C) gave ϵ' values comparable to those of the unannealed commercial α-Fe_2O_3 powder materials. The mechanism responsible for this variation of ϵ' is not completely understood; the data appear to be consistent with a hypothesis that defects introduced into the structure upon annealing at high temperatures cause "local variations in the Morin temperature." The apparent reduction in quadrupole interaction would then result from a small admixture of "$\epsilon'=+\frac{1}{4}e^2qQ$" into the dominant "$\epsilon'=-\frac{1}{8}e^2qQ$." This problem is under further investigation; results will be reported separately.

There was no significant difference in ϵ' obtained for materials from the different suppliers or for the synthetic crystals, provided the last heat treatment was below 950°C. In view of the above remarks, the weighted average value of ϵ' from our data (excluding those from the high-temperature annealed samples) gives a quadrupole coupling constant

$$e^2qQ=+0.880\pm0.024 \text{ mm/sec.}$$

To make optimum use of all data available, the determination of ϵ' from the positions of all *six* lines, Eq. (3), is preferred to the frequently used outer-four-line method. Since the calculation of ϵ' effectively involves small differences of large numbers, extensive measurements were made to obtain corrections for slight nonlinearities in the drive system. This procedure included making independent measurements with four ME spectrometers different in design and/or operating mode. For the main (loudspeaker) spectrometer, correction factors were obtained by phase shifting (by 180°) the velocity signal and by varying the drive amplitude significantly. The value of e^2qQ given above includes a total correction of $\approx 6\%$ (downward).

III. α-Fe_2O_3 STRUCTURAL PARAMETERS

Recently, very accurate structural parameters for α-Fe_2O_3 have been published by Blake and co-workers[8] (denoted by BHZF in the following). These results, obtained from x-ray diffraction intensity measurements on a natural hematite crystal, were very similar to those of Nordmark[19] for synthetic crystals of pure α-Fe_2O_3. They do differ somewhat from the structural parameters[7] used in JOA for the determination of Q. The mineral crystal used for the BHZF measurements contained appreciable amounts of impurities (by weight, 1.0±0.2% Al, 0.10±0.02% Ti, and 0.021±0.005% Cr) which can replace iron in the α-Fe_2O_3 corundum structure. A ME study of this same material[20] showed somewhat broadened lines and an apparent quadrupole interaction about a *factor of* 3 times smaller than that of the pure material. The isomer shift and internal magnetic field were essentially the same as for the pure material.

The large ME differences between the natural and synthetic materials (and the sensitivity of the EFG calculations to slight variations in the structural parameters) raised certain doubts about the use of the BHZF parameters, which appeared to be the "best" available at that time. Blake and his collaborators agreed to do a new structure refinement on pure synthetic single-crystal specimens[16] and to improve simultaneously the accuracy of their measurements. These results[21] (denoted as BFZ in the following) are given in the first line of Table I, where the other structural-parameter data are summarized. The notation is as defined in Ref. 8, with a_h and c_h the a- and c-axis lattice constants (hexagonal representation), and x(O) and z(Fe) the oxygen and iron special position parameters.

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[19] C. Nordmark (private communication from S. Åsbrink, University of Stockholm).

[20] We thank R. L. Blake for providing samples of his mineral specimens.

[21] R. L. Blake, L. W. Finger, and T. Zoltai, denoted as BFZ in text. A note will be submitted to Am. Mineralogist.

TABLE II. $Q(\mathrm{Fe}^{57m})$ and contributions to the EFG in α-$\mathrm{Fe_2O_3}$ for various structure parameters. Quantities and units are as defined in the text or in Ref. 1.

		α-$\mathrm{Fe_2O_3}$ structure-parameter variations[a]								
Quantity	Units	BFZ[b]	BFZ (δa)	BFZ (δc)	BFZ (δx^-)	BFZ (δx^+)	BFZ (δz^-)	BFZ (δz^+)	JOA[c]	SD[d]
a_h	Å	5.035[e]	*5.038*	5.035	5.035	5.035	5.035	5.035	*5.0345*	*5.0328*
c_h	Å	13.752	13.752	*13.772*	13.752	13.752	13.752	13.752	*13.749*	*13.751*
$x(\mathrm{O})$		0.3072	0.3072	0.3072	*0.305*	*0.309*	0.3072	0.3072	*0.300*	*0.302*
$z(\mathrm{Fe})$		0.3553[e]	0.3553	0.3553	0.3553	0.3553	*0.3550*	*0.3555*	*0.355*	*0.355*
E_{Fe}	10^6 dyn/esu	0.27469	0.27382	0.27605	0.20403	0.33210	0.27539	0.27423	0.04269	0.10750
E_{O}	10^6 dyn/esu	−0.06589	−0.06393	−0.07049	−0.06482	−0.06705	−0.03964	−0.08335	−0.03664	−0.03859
K_1	10^{24} cm^{-3}	0.09032	0.08999	0.09074	0.09032	0.09032	0.08986	0.09062	0.08986	0.09009
K_2	10^{24} cm^{-3}	−0.66161	−0.66084	−0.66063	−0.66684	−0.65733	−0.66325	−0.66052	−0.68075	−0.67632
K_3	10^{24} cm^{-3}	−0.44108	−0.44056	−0.44042	−0.44456	−0.43822	−0.44217	−0.44035	−0.45384	−0.45088
K_4	10^{24} cm^{-3}	−0.03358	−0.03335	−0.03401	−0.03909	−0.02914	−0.03358	−0.03358	−0.05191	−0.04691
$eq_{d\text{-}\mathrm{Fe}}'$	10^{32} esu	−0.05504	−0.05516	−0.05452	−0.05504	−0.05504	−0.05640	−0.05416	−0.05644	−0.05636
$eq_{d\text{-}\mathrm{O}}'$	10^{32} esu	−0.39736	−0.39676	−0.39656	−0.40980	−0.38736	−0.39588	−0.39836	−0.43792	−0.42632
eq_m'	10^{14} esu	0.42422	0.42806	0.41299	0.38126	0.45838	0.41648	0.42956	0.27247	0.31079
eq_d'	10^{14} esu	0.06941	0.06728	0.07402	0.06940	0.06967	0.04160	0.08802	0.04056	0.04212
eq'	10^{14} esu	0.49363	0.49534	0.48701	0.45066	0.52805	0.45808	0.51758	0.31303	0.35291
$Q(\mathrm{Fe}^{57m})$[f]	$b(10^{-24}$ cm$^2)$	0.2819	0.2810	0.2858	0.3088	0.2636	0.3038	0.2689	0.4446	0.3943

[a] Structure-parameter variations from the BFZ values are printed in italic type.

[b] Reference 21, but see footnote e.

[c] Reference 1 (i.e., from Ref. 7).

[d] Values adopted by Sharma and Das, Ref. 4. As sources, these authors quote Newnham and de Haan (Ref. 7) and Cox and Shirane [private communication reported by G. Burns, Phys. Rev. 124, 524 (1961)]; their a_h is apparently from this latter source, and their x and z are apparently from Ref. e of the present Table I, but the origin of their value for c_h is not clear.

[e] For convenience, parameter values have been rounded off from the BFZ values given in Table I. However, the Q and eq' values quoted in the text have been corrected (by interpolation) to correspond to the unrounded parameters.

[f] All calculated with $e^2qQ = 0.880$ mm/sec and $\gamma_\infty = -9.14$. The oxygen polarizability is $\alpha_{\mathrm{O}} = 2.91$ Å^3 for all calculations in the table.

It is interesting to note that, although there is such a large change in the apparent quadrupole interaction,[22] there is very little difference in the structure parameters (especially for x and z) between the BFZ determination for the synthetic material and the BHZF results for the natural material.

The significant difference between the BFZ structural data adopted for the EFG calculation and the older data[7] used in JOA is in the value of the oxygen special position parameter, which is ~2% higher in the newer data.

IV. EFG CALCULATIONS

The method employed for the EFG calculation, and the notation and units, are as described in JOA. The oxygen dipole polarizability is taken into account, while the iron polarizability is assumed to be negligible. Thus the unshielded field gradient (principal component of EFG tensor) at the iron site, eq', is determined from Eq. (3) of JOA.[23] We use the same polarizability value, $\alpha_O = 2.91$ Å^3, because there is no reason to prefer any other. (See Sec. V for additional comments on α_O.)

Using the BFZ parameters,[21] we obtain for eq' the value $+4.910\times10^{13}$ esu; the monopole contribution to the EFG, eq_m', is $+4.232\times10^{13}$; and the dipole contribution eq_d' is $+0.6785\times10^{13}$ esu. With

$$e^2qQ\ [\equiv e^2q'(1-\gamma_\infty)Q] = +0.880 \text{ mm/sec}$$

and $\gamma_\infty = -9.14$ for the antishielding factor,[5,24] we obtain

$$Q(Fe^{57m}) = +0.283 \text{ b}.$$

To estimate the effect of slight variations in the structure parameters on the resultant Q, field-gradient calculations have also been made with small departures from the BFZ structure parameters. The results of some of these calculations are given in Table II. A much more extensive table is available from one of the authors (JOA).

TABLE III. Sensitivity of $Q(Fe^{57m})$ to structural-parameter variations, $S = (\partial Q/\partial p)/(Q/p)$.

p	S
a_h	-5.7
c_h	$+9.4$
x (O)	-11.8
z (Fe)	-88.0

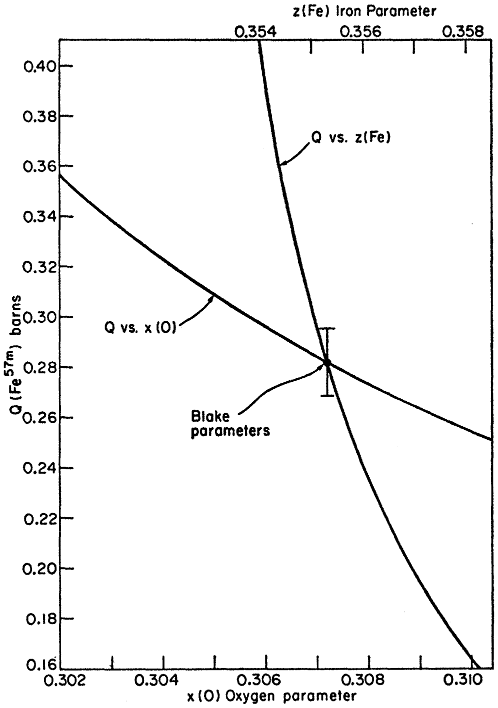

FIG. 2. Variation of $Q(Fe^{57m})$ resulting from changes of structure parameters from the BFZ values (with $e^2qQ = +0.880$ mm/sec). Separate curves are shown for changes in x(O) and z(Fe), respectively, the other parameters remaining fixed at the BFZ values. The error flag reflects the uncertainty in Q resulting from the combined uncertainties in x and z.

The sensitivity S of the resultant Q to the various parameter changes has been calculated from these data in terms of the "logarithmic derivatives" for the independent variation of the several parameters p about the BFZ values: thus for $Q = Q(a_h, c_h, x, z)$, we have $S = (\partial Q/\partial p)/(Q/p)$. The results are summarized in Table III. For comparison, the corresponding S for the oxygen polarizability parameter is $S(\alpha_O) = -0.136$.

From Table III it is seen that the derived value of Q is extremely sensitive to changes in z(Fe) and moderately sensitive to changes in x(O). Figure 2 shows the Q obtained for independent variations of z and x. The lattice constants a_h and c_h have relatively less influence on the value obtained for Q. Since changes in these parameters shift Q in opposite directions, there will be a partial canceling of scaling-type systematic errors.

V. UNCERTAINTY IN $Q(Fe^{57m})$

To arrive at an estimate of the over-all uncertainty in Q, we assume independence of variables and determine the variance of Q resulting from the uncertainty in each parameter taken independently. The over-all variance is taken as the sum of the individual variances. The standard deviations for the BFZ structural parameters in Table I are for internal consistency as de-

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[22] As in the case of the annealing experiments, this change probably results from a partial change in magnetic ordering (near the impurities) rather than from a direct change in the EFG. In his detailed ME study of α-Fe_2O_3, F. van der Woude [Phys. Status Solidi **17**, 417 (1966)] examined mineral material near the Morin temperature and concluded that two spin configurations (and two slightly differing effective magnetic fields) existed simultaneously in it.

[23] The present notation trivially differs from that in JOA by a factor of e (i.e., the former "q" is given as "eq" here). Also, the equal sign in Eq. (3) of JOA should be replaced by a plus sign.

[24] R. M. Sternheimer, Phys. Rev. **80**, 102 (1950); **84**, 244 (1951); H. M. Foley, R. M. Sternheimer, and D. Tycko, *ibid.* **93**, 734 (1954).

termined by computer analysis.[8,21] It has been estimated[25] that the over-all uncertainties (external and internal) are roughly double the stated values. Thus the uncertainties in Table I, somewhat arbitrarily increased by a factor of 2 and combined with the sensitivities in Table III, give the following contributions to the uncertainty in Q: a_h, 0.18%; c_h, 0.41%; $x(\mathrm{O})$, 5.38%; and $z(\mathrm{Fe})$, 3.96%. The experimental uncertainty in e^2qQ is 2.73%. The upper limit on the uncertainty in γ_∞ has been estimated[26] as 10%, which would introduce a 9% uncertainty in Q.

The uncertainty in the polarizability is most difficult to estimate. Values reported in the literature for the oxygen polarizability in various metallic oxides range between about 1 and 3.5 Å.[3] For example, Taylor and Das[27] in a detailed paper on polarizability obtained $\alpha_{\mathrm{O}}=2.19$ Å^3 in BeO, while Rao and Rao[28] found $\alpha_{\mathrm{O}}=1.0$ Å^3 to give the best agreement between measured and calculated (lattice-sum) field gradients for chrysoberyl. The early classic paper of Tessman *et al.*[29] summarizes other α_{O} data. The value adopted here, 2.91 Å^3, is calculated[1] from the α-$\mathrm{Fe_2O_3}$ refractive index using the Clausius-Mosotti relation. In view of all these variations, we shall assume a 35% uncertainty (±1 Å^3) in α_{O}, which contributes a 4.76% uncertainty to Q.

When all the variances corresponding to the above "standard deviations" are combined linearly, the over-all uncertainty in Q is 12.5% and thus

$$Q(\mathrm{Fe}^{57m})=+0.283\pm0.035\ \mathrm{b}.$$

The uncertainty resulting from the calculation procedure has not been included explicitly above; it is negligible[1] in comparison to the other uncertainties. Of course, also not included are uncertainties resulting from phenomena not treated in the present model, such as quadrupole (and higher) polarizability and covalency.

VI. DISCUSSION

There are two differences between lattice calculation results based on the BFZ parameter values and those of JOA: The monopole contribution to the EFG increased by 56%; and the electric field at the oxygen positions increased by 80%, causing the oxygen dipolar contribution to the EFG to rise correspondingly. (The electric field at the Fe site increased fivefold; however, we are neglecting Fe dipolar contributions as heretofore, since the Fe polarizability is expected to be small.) Thus, the oxygen polarizability is more important now than in JOA. The major change in the resulting Q is caused by the relatively large change in $x(\mathrm{O})$ from the value[7] previously used. In a preliminary report of the present work,[9] a value $Q=+0.300\pm0.035$ b was obtained using the same ME data but the BHZF instead of the BFZ structure parameters. Despite the large differences in the measured ϵ's for the natural and synthetic crystals, it is worth noting that the calculated EFG's are nearly equal. This suggests that the effect of the impurities is not primarily a change in the EFG.[22]

Several previous works have noted the sensitivity of the calculated EFG for various structures to changes in the special position parameters. Vaughan and Drickamer,[30] for example, using essentially the same method as the present work, calculated variations of eq' around the Newnham–de Haan[7] parameters as a base point to help interpret their high-pressure α-$\mathrm{Fe_2O_3}$ ME data.

The present value of $Q(\mathrm{Fe}^{57m})$ now agrees with that of Sternheimer[5] and Sharma and Das[4] in α-$\mathrm{Fe_2O_3}$, but this is undoubtedly fortuitous.[31] The close matching of Ingalls' (Fe^{2+}) result is perhaps more remarkable in view of the uncertainties in both determinations, which are quite different in approach. From measurements and EFG calculations for a series of (Fe^{3+}) garnets, Nicholson and Burns[32] concluded $Q\approx+0.2$ b; however, they did not include polarizability and, probably more important, they used room-temperature structure parameters and high-temperature (~600°K) measurements of e^2qQ. Based on α-FeOOH (ferric), van der Woude and Dekker[33] obtained $Q=+0.28$ b; however, they calculated only the monopole contribution, used high-temperature e^2qQ data, and assumed that crystallographic special position parameters obtained for α-AlOOH could be used for α-FeOOH. Assuming $Q=+0.18$ b, Bhide and Multani[34] found good agreement for measured and calculated EFG's for source experiments with Fe^{3+} in $\mathrm{BaTiO_3}$. They included polarizability and assumed an ionicity of 60% (based on isomer-shift data). Although Hudson and Whitfield[35] did not directly determine Q in their work on the ferrites, their calculations

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[25] L. Finger (private communication).

[26] R. M. Sternheimer (private communication). Reference 5 states that $\gamma_\infty(\mathrm{Fe}^{3+})$ is accurate to ~5% for the given Hartree-Fock wave functions used in the calculation. The 10% figure in addition allows for the uncertainty in the wave functions as well as the fact that the Fe^{3+} ion is not isolated but is located in a crystal lattice [i.e., we assume $\gamma_\infty(\mathrm{Fe_2O_3})\approx\gamma_\infty(\mathrm{Fe}^{3+})$]. The papers cited in Refs. 5 and 24 should be consulted for additional information.

[27] T. T. Taylor and T. P. Das, Phys. Rev. **133**, A1327 (1964).

[28] L. D. V. Rao and D. V. G. L. N. Rao, Phys. Rev. **160**, 274 (1967).

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

[30] R. W. Vaughan and H. G. Drickamer, J. Chem. Phys. **47**, 1530 (1967).

[31] Sternheimer calculated an improved value for γ_∞ and used this to correct a very rough early estimate, $Q\approx+0.4$ b, by Burns [G. Burns, Phys. Rev. **124**, 524 (1961)], which was based on point-charge lattice-sum calculations for YIG and α-$\mathrm{Fe_2O_3}$. In JOA it was suggested that Sharma and Das, based on their input structure data, incorrectly calculated the parameters equivalent to those listed in the present Table II. For comparison purposes we therefore explicitly list in Table II the values *we* obtain starting from these data. The numbers are quite distinct from the ones we obtain from the BFZ data. The agreement between the Sharma and Das Q result, as deduced from the calculations in *their* paper, and ours thus clearly is accidental and of no particular significance.

[32] W. J. Nicholson and G. Burns, Phys. Rev. **133**, A1568 (1964).

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

[34] V. G. Bhide and M. S. Multani, Phys. Rev. **139**, A1983 (1965).

[35] A. Hudson and H. J. Whitfield, Mol. Phys. **12**, 165 (1967).

(similar to the present method, including dipole terms) suggest better agreement when only the monopole terms are used; thus they speculate that the dipole terms are to a large extent canceled by induced quadrupole moments and "covalency" which were not included in their calculations.

Very recent determinations of Q based on ferrous-compound data for different compounds and using different methods of calculation are considerably more consistent ($Q \approx +0.2$ b) than the above-mentioned results for ferric compounds. From a study of $FeSiF_6 \cdot 6H_2O$ (the same ferrous compound used by Ingalls), Nozik and Kaplan[11] obtained $Q = +0.20$ b. Their calculation differs from Ingalls' in two respects: (1) They disagree in the lattice contribution to the EFG, and (2) Ingalls applies a covalency correction to the valence contribution while Nozik and Kaplan do not. Such a covalency correction would *increase* their value for Q. Also, using this same material, Johnson[12] found $Q = +0.18$ b by a clever approach in which anisotropic hyperfine interactions were used to determine $\langle r^{-3} \rangle$ (averaged over the $3d$ wave functions). By assuming that the $\langle r^{-3} \rangle$ for the quadrupole interaction was the same as experimentally determined by the magnetic interaction, he obtained a value for Q with the screening and covalency correction (25%) automatically included. Ham's[13] calculations of the strain-induced crystal-field splitting for Fe^{2+} in MgO combined with Leider and Pipkorn's[36] ME measurements on the same system indicate that $Q \approx +0.2$ b.

From molecular-orbital calculations and experiments on a series of (ferrous and ferric) hemoglobin compounds, Weissbluth and Maling[37] suggest that $Q = 0.17$ b. It is interesting that when they separate their data for ferrous versus ferric compounds, the latter imply a Q about a factor of 2 larger than the former. They comment that the discrepancy could result from the different shielding factors used.

The nuclear-model calculations (Coriolis coupling of two rotational bands) of Sood and Hutcheon[38] indicate that $Q = 0.16 \pm 0.02$ b, but in their present state of refinement nuclear-model calculations cannot be expected to give very reliable values. Indeed, the agreement between their calculated and independent experimental values for magnetic moments and for reduced transition probabilities is not particularly good.

In light of the current information available, the inclusion of covalency effects in the evaluation of Q from ferric-compound data appears to be quite difficult and uncertain.[39]

VII. CONCLUSIONS

The 14.4-keV excited-state quadrupole moment based on ME measurements and lattice-sum EFG calculations in α-Fe_2O_3 (including dipole polarizability and antishielding corrections) is found to be $Q(Fe^{57m}) = +0.283 \pm 0.035$ b. The discrepancies among the more recently obtained values for Q apparently can be removed only by making significant improvements in the models used to obtain the EFG's.

As demonstrated in the present as well as in other studies, the calculated EFG is *very* sensitive to slight changes in the structural parameters. Consequently, because of slight (even local) structural differences, substantial uncertainties may be present in Q's derived from the ratio of measured quadrupole coupling constants and a known moment. Significant variations in the measured quadrupole coupling constant apparently can result from the sample preparation procedure. It follows that, once a reliable value of the quadrupole moment is available, e^2qQ measurements (e.g., by ME spectroscopy) can provide a valuable tool for structural investigations.

The extreme sensitivity of Q to z(Fe) and the relatively small magnitude of the quadrupole interaction at the Fe site in α-Fe_2O_3 suggest that other ferric compounds may be more suitable for Fe^{57m} quadrupole-moment determinations. In any case, evaluations of Q for Fe in a number of environments, and particularly for a series of isostructural compounds, would be of use in settling some of the questions raised about covalency, polarizability, and shielding.

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The EFG calculations were performed on an IBM 7040, then at the Carnegie-Mellon University Computation Center.

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[36] H. R. Leider and D. N. Pipkorn, Phys. Rev. **165**, 494 (1968).

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

[38] P. C. Sood and D. A. Hutcheon, Nucl. Phys. **A96**, 159 (1967).

[39] Several helpful discussions of covalency questions with E. Šimánek are very much appreciated.