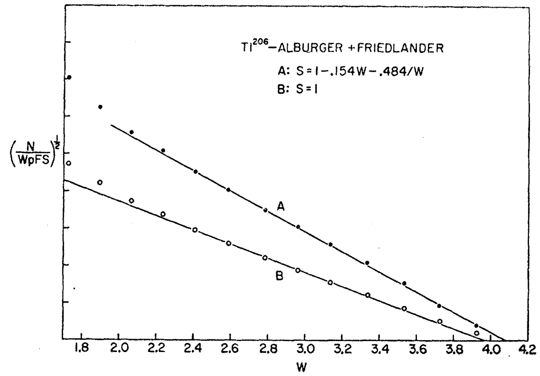

FIG. 8. Fermi-Kurie plot of Tl^{206} data reported by Alburger and Friedlander. Curve B shows the conventional plot of the data. Curve A shows a plot after the application of the shape factor found in this investigation. The data now extrapolate to a higher end point in good agreement with the value found in the present study.

CONCLUSION

The beta spectrum of Tl^{206} has been measured and was found to have a nonstatistical shape. The data are fitted by a pure pseudovector shape factor

$$S=1-0.154W-0.484/W.$$

No pseudoscalar contribution is needed in order to fit the spectrum.

With the measured energy release 1.571 ± 0.010 Mev it is possible to make a better determination of the first-excited state of Bi^{210}. Using the energies reported by Golenetskii *et al.*[12] the long-lived metastable state of Bi^{210} is found to be 301 ± 10 kev above the ground level.

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Nuclear Quadrupole Moment of Fe^{57m}

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A value for the nuclear quadrupole moment of the excited state of iron, Q^{57m}, is obtained using published values for eQq/h in the octahedral and tetrahedral sites in $Y_3Fe_2(FeO_4)_3$ (YIG) and in Fe_2O_3, along with recent values for the atomic coordinates in these compounds. The value of Q^{57m} is definitely positive and $\approx+0.4\times10^{-24}$ cm^2.

INTRODUCTION

THE Mössbauer effect[1] enables one to obtain values of the nuclear quadrupole coupling constant, eQq/h. This quantity is a measure of the interaction of the nuclear quadrupole moment, Q, with the second derivative of the electrostatic potential along a particular crystal direction, q. Kistner and Sunyar[2] were the first to measure eQq/h of the excited nuclear state of iron 57, Fe^{57m}. The excited state has a nuclear spin, I, of $\frac{3}{2}$ and can thus possess a nonzero Q.

In this paper an estimate of Q^{57m} is made using the following published data for eQq/h: measurements of Fe in both Fe_2O_3 by Buchanan and Wertheim,[3] and in the octahedral and tetrahedral sites in $Y_3Fe_2(FeO_4)_3$ (YIG) by Alff and Wertheim.[4] In all of these cases the iron is in a $+3$ valence state. This simplifies the calculation since the outer electron configuration is a half-filled $3d$ configuration; thus the unperturbed core contribution to q is zero. The contribution to q then arises from the other ions in the lattice. One can then obtain q as follows:

$$q=(1-\gamma_\infty)\sum_i\left(\frac{3\cos^2\theta_i-1}{r_i^3}\right)e_i\equiv(1-\gamma_\infty)q_u, \qquad (1)$$

where γ_∞ is the antishielding factor,[5] r_i is the distance to the ith charge, θ_i is the angle between the principal axis of the field gradient tensor and r_i, e_i is the charge of the ith ion and the sum is over all the ions in the lattice except the one at $r=0$. The antishielding factor for Fe^{+3} has already been calculated.[6] The lattice sum is calculated on an IBM 704 using a program developed by Bersohn.[7]

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TABLE I. Contributions to the unshielded field gradient, q_u, at the Fe^{+3} (a) and (d) sites in YIG. The x-ray data of Geller and Gilleo[11] were used.

Field gradient produced by	Field gradient at Fe (a) along ⟨111⟩	Field gradient at Fe (d) along ⟨100⟩
Oxygen 96(h) ($x=-0.0274$, $y=+0.0572$, $z=+0.1492$)	$+256.910(-2e)$[b]	$+255.680(-2e)$
Iron 24 (d) (tetrahedral site)[a]	$-167.723(+3e)$	$-35.165(+3e)$
Yttrium 24 (c)[a]	$+167.723(+3e)$	$+173.057(+3e)$
Iron 16 (a) (octahedral site)	$0.0(+3e)$	$-48.510(+3e)$
Total q_u obtained by adding the contributions listed and dividing by the lattice constant, a cubed. $a=12.376$ A; $e=4.8029\times10^{-10}$ esu.	$-1.3019\times10^{+14}$ esu/cm^3	$-0.6163\times10^{+14}$ esu/cm^3

[a] See reference 14.
[b] To obtain q_u of oxygen, etc., one must multiply $+256.9$ etc. by the charge $(-2e)$ etc. and divide by the lattice constant, a, cubed.

RESULTS

Previous Calculations

There have been two independent estimates of Q^{57m} using Eq. (1) and early incorrect values of eQq/h for Fe_2O_3.[2] Bersohn assumed that the difference in the internal atomic coordinates between Fe_2O_3 and Al_2O_3 would have a small effect on the lattice sum in Eq. (1). Thus, he applied the Al_2O_3 results to Fe_2O_3.[8] However, q is sensitive to the internal coordinate and, as has been calculated,[6] one obtains a very small q for Fe_2O_3 (4.23 times smaller than for Al_2O_3) making Q^{57m} very large ($\approx-1\times10^{-24}$ cm^2). If one, however, considers the error in the x-ray coordinates[9] used in these calculations, either a + or − value can be obtained for Q^{57m} as has been pointed out previously.[6] The situation has changed since these calculations were made. The value of eQq/h in Fe_2O_3 has been remeasured and reinterpreted[3] so that it is larger and now positive in sign and the internal coordinates of Fe_2O_3 have been re-evaluated by modern techniques.[10] Also, data exist for eQq/h for Fe^{+3} in two different sites in YIG[4] and structure of this material is known.[11]

$Y_3Fe_2(FeO_4)_3$ (YIG)

Alff and Wertheim[4] have measured eQq/h for Fe^{57m} in the octahedral (a) and tetrahedral (d) sites to be −22 Mc/sec and −18 Mc/sec, respectively. Geller and Gilleo[11] have measured the internal atomic coordinates of the ions in YIG. Using these x-ray data, the lattice sum of Eq. (1) is calculated and the result can be seen in Table I. Since there are 160 atoms in the unit cells, care was taken to use symmetry to reduce the number of calculations required. The point symmetry of the (a) site is $\bar{6}$ and that of the (d) site is $\bar{4}$, so one need carry out no more than $\approx\frac{1}{6}$ and $\approx\frac{1}{4}$ of 160 sums for the two respective sites. By dividing the above-quoted values of eQq/h by the lattice sum in Table II and by $(1-\gamma_\infty)$, where $\gamma_\infty=-6.17$,[6] one obtains $Q^{57m}=+0.325\times10^{-24}$ and $+0.562\times10^{-24}$ cm^2 for the (a) and (d) sites, respectively.

The values of q_u in Table I are obtained by summing the contributions from the ions within a sphere with radius five times the lattice constant. Extending the radius to six lattice constants increases the values for q_u in Table I by $\approx0.3\%$. The error in q_u due to the error in the x ray coordinates of the oxygen ions was also considered. The x, y, z parameters were varied within the ±0.0002 limit of error[11] to give the maximum q_u for Fe(a). The q_u increased by $\approx2\%$.[12] Thus, the error in q_u due to the convergence or the inaccuracy of the x-ray parameters is small. The model is a pure ionic one and neglects any covalent effects of the Fe^{+3} ions contributing to q as well as these effects contributing to charge distribution on other ions. Also neglected is the contribution to q due to the higher moments of the ions[13] (i.e. dipole moment of the O^{-2} ions). Nevertheless, the difference between values of Q^{57m} obtained from the two sites is almost within the $\pm20\%$ error in the experimental measurements.[4] Note that the contribution to q at Fe (a) arises only from the O^{-2} ions while all the ions contribute to q at Fe (d).[14]

Fe_2O_3

Buchanan and Wertheim[3] have remeasured eQq/h of Fe^{57m} in Fe_2O_3 correctly taking into account the direction of the internal field with respect to the principal axis of the field gradient tensor. At room temperature, they obtain $eQq/h=+10$ Mc/sec and at low temperatures, when the internal field is along the ⟨111⟩ direction, they obtain $+8.5\pm10\%$ Mc/sec. The low temperature data gave a better fit.[3] Normally, one would want to use the room temperature data since the coordinates of the

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[9] L. Pauling and S. B. Hendricks, J. Am. Chem. Soc. 47, 781 (1925).
[10] D. E. Cox and G. Shirane (private communication).
[11] S. Geller and M. A. Gilleo, J. Phys. Chem. Solids 3, 30 (1957).
[12] After the lattice sum for YIG was carried out, using the atomic coordinates given in reference 11, a more recent paper by the same authors on the atomic parameters in YIG came to my attention [J. Phys. Chem. Solids 3, 30 (1959)]. These new atomic parameters are very close to the older ones and the q_u that would result would be within the 2% quoted in the text.
[13] G. Burns, Phys. Rev. **115**, 357 (1959).
[14] The 24 (c) and (d) sites taken together form a cubic lattice with respect to the 16 (a) sites. However, the contribution from each lattice position is listed in Table I since it might be useful for other garnets which have ions with different charges in the (c) and (d) sites.

TABLE II. Contributions to the unshielded field gradient, q_u, at the Fe^{+3} sites in Fe_2O_3. The u and x values of Cox and Shirane obtained by neutron diffraction were used.[10]

Field gradient produced by		*Field gradient at Fe along ⟨111⟩*
Iron 4 (c)	$\pm(u,u,u)$ $\pm(\frac{1}{2}+u, \frac{1}{2}+u, \frac{1}{2}+u)$	$-0.8654(+3e)$[a]
Oxygen 6 (c) $u=0.355$; $\alpha=55°17'$; $x=0.552$; $a=5.424$ Å.	$\pm(x, \frac{1}{2}-x, \frac{1}{4})C$	$-6.2851(-2e)$
Total q_u obtained by adding the contribution listed and dividing by a^3		$+2.9240\times10^{13}$ esu/cm^3

[a] To obtain q_u of oxygen, etc., one must multiply $+256.9$ etc. by the charge $(-2e)$ etc. and divide by the lattice constant, a, cubed.

ions were measured at room temperature. However, it is known that eQq/h of Al in Al_2O_3 is independent of temperature between 4.2° and 300°K.[15] Similar results would be expected in the isomorphous compound Fe_2O_3. Since little change of eQq/h with temperature is thus expected and since the low temperature data gives a better fit the value used here is $eQq/h=+9.0$ Mc/sec.

Cox and Shirane[10] have measured the atomic coordinates of the ions in Fe_2O_3 using neutron diffraction techniques. Their results are undoubtedly more accurate than the very old x-ray results that were used previously.[6,8] The lattice sum was carried out with the more recent data and the results can be seen in Table I. By dividing the above-mentioned value of eQq/h by the value for the sum in Table III and $(1-\gamma_\infty)$,[6] one obtains $Q^{57m}=+0.592\times10^{-24}$ cm^2.

Again, the lattice sum in Table II was obtained by summing the contributions within a sphere with a radius five times the lattice constant. Extending the radius one more lattice constant causes q to increase $\approx0.7\%$. A much larger error is found when one considers that the parameter describing the oxygen positions is $x=0.552\pm0.003$.[10] Taking $x=0.555$, one obtains $Q^{57m}=+0.487\times10^{-24}$ cm^2. Adding $\pm10\%$ to this from the quadrupole measurements, one can obtain as small a value as $Q^{57m}=+0.44\times10^{-24}$ cm^2.[16]

CONCLUSION

The values of Q^{57m} obtained for the 16 (a) and 24 (d) sites in YIG and the 4 (c) sites in Fe_2O_3 are $+0.33\times10^{-24}$, $+0.56\times10^{-24}$, and 0.59×10^{-24} cm^2, respectively. When the limits of error of eQq/h in YIG and eQq/h and the atomic coordinates in Fe_2O_3 are considered, one can obtain extreme values for Q^{57m} of $+0.39\times10^{-24}$, $+0.45\times10^{-24}$, and $+0.44\times10^{-24}$ cm^2, respectively, which almost overlap. This is as good as can be expected for this type of calculations where three different sets of data are considered.

Thus, Q^{57m} is definitely positive and $\approx+0.4\times10^{-24}$ cm^2.

Note added in proof. In a recent publication Abragam and Boutron [Compt. rend. **252**, 2404 (1961)] have also pointed out that eQq/h must be positive in Fe_2O_3 because the spins are perpendicular to the c axis at room temperature rather than parallel. They also obtain a value for Q^{57m} from Fe^{+2} in FeF_2.

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[16] Besides obtaining Q^{57m} by dividing the measured eQq/h by $(1-\gamma_\infty)$ and by the calculated q_u one could also obtain it by taking the ratio of the results in Fe_2O_3 to those in Al_2O_3 as was done in references 6 and 8. Instead of $+0.59\times10^{-24}$ cm^2 one would obtain 0.34×10^{-24} cm^2. Although this method may eliminate some of the error due to the dipole and other moments on the O^{-2} ion it compounds the error due to the uncertainties in the atomic coordinates. Unless one is more certain of the Al_2O_3 x-ray data it appears that dividing the measured eQq/h by the calculated $(1-\gamma_\infty)$ and q_u should give a reasonable value for Q.