

Electric Quadrupole Moment of the 14.4-keV State of Fe^{57}

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From a measurement of the Mössbauer absorption spectrum of ferrous fluosilicate for polarized 14.4-keV radiation, the quadrupole moment of the first excited state of Fe^{57} is deduced to be $+0.12$ b. This value is subject to a small correction due to the internal Sternheimer effect for the Fe^{++} ion.

INTRODUCTION

AN effect on the hyperfine structure associated with the nuclear quadrupole moment of the first excited state of Fe^{57} was first observed by Kistner and Sunyar¹ in a study of the Mössbauer effect of Fe^{57} in Fe_2O_3 . Bersohn² deduced from this result a quadrupole moment $Q = -0.19$ b, but his analysis has been questioned by Burns and Wikner,³ by Abragam and Boutron,⁴ and by Burns.⁵ Abragam and Boutron pointed out that the sign of Q is probably positive and Burns gave a value $Q \cong +0.4$ b. Measurements by Wertheim⁶ on FeF_2 again showed a quadrupole effect, and Abragam and Boutron have analysed this result to give $Q = +0.09$ b. DeBenedetti, Lang, and Ingalls⁷ have estimated the magnitude of Q to be about 0.1 b from measurements on several Fe^{++} salts.

We have made measurements on ferrous fluosilicate, $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$, following a suggestion by Bleaney⁸ who pointed out that the orbital ground state of the paramagnetic ferrous ion in this salt is simple.⁹⁻¹¹ The electric field gradient is produced by the charge distribution on the ferrous ion and may be calculated from the ground-state wave function. Furthermore, the Sternheimer correction factor,¹² which takes account of the distortion of the ion core, appears to be small when the electric field gradient arises from an internal charge asymmetry. We have measured the quadrupole splitting by employing the now familiar techniques of velocity spectrometry. In addition, by using a source of polarized γ rays we were able to measure the polarization of the two components of the spectrum and hence to determine the sign of the quadrupole coupling directly. From the calculated value of the electric field gradient both the

sign and magnitude of the quadrupole moment may be deduced.

APPARATUS

The velocity spectrometer was constructed in the Argonne National Laboratory shops chiefly by E. Kolacek. Its principle of operation is shown by the schematic diagram of Fig. 1. The lead-screw L is caused to rotate by the O-ring drive and reversible synchronous motor thereby transporting the carriage back and forth a distance of about 2 in. as determined by reversing limit-switches. The plane P, whose inclination to the lead-screw axis is variable by the micrometer M, moves along with the carriage and causes the table T supported on ball bearings to move back and forth at constant speed along ways perpendicular to the screw axis. The table is held to the plane by adhesion in the thin oil film separating the finely surfaced plane from a sliding shoe S fastened to the table. The table speed is proportional to the tangent of the angle of inclination of the plane, and hence is a linear function of the micrometer reading. The pulley sizes are chosen so that a 0.001-in. change on the micrometer alters the table velocity by 0.001 cm/sec.

In the present experiments the table carried the source. For measurements of the splitting, Co^{57} diffused in copper was used to produce a monoenergetic γ ray. For the determination of the sign, polarized γ rays were produced using Co^{57} diffused in iron foil which was magnetized in a field of about 800 oe. The magnet and foil assembly could be rotated in the plane of the foil so

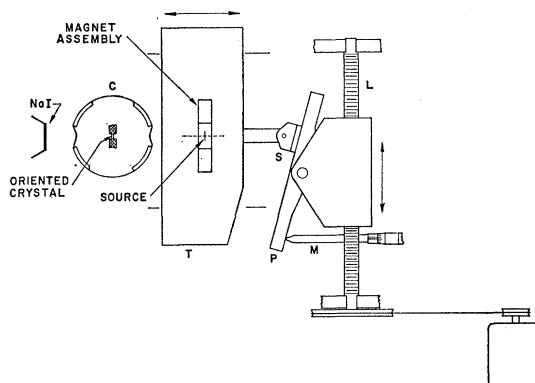


FIG. 1. Schematic diagram of the velocity spectrometer. L, lead-screw; M, micrometer; P, inclined plane; S, sliding shoe; T, table; C, cryostat.

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¹ O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters 4, 412 (1960).

² R. Bersohn, Phys. Rev. Letters 4, 609 (1960).

³ G. Burns and E. G. Wikner, Phys. Rev. 121, 155 (1961).

⁴ A. Abragam and F. Boutron, Compt. rend. 252, 2404 (1961).

⁵ G. Burns, Phys. Rev. 124, 524 (1961).

⁶ G. K. Wertheim, Phys. Rev. 121, 63 (1961).

⁷ S. DeBenedetti, G. Lang, and R. Ingalls, Phys. Rev. Letters 6, 60 (1961).

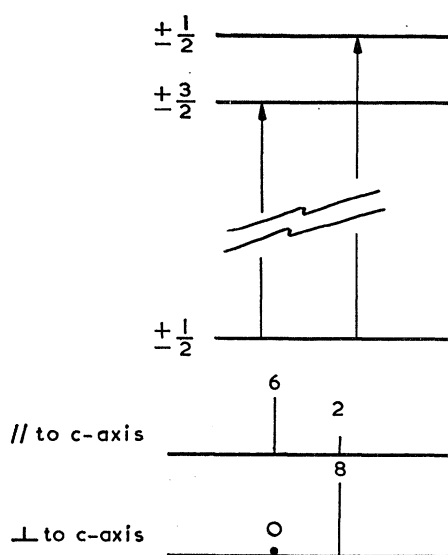
⁸ B. Bleaney (private communication).

⁹ L. C. Jackson, Phil. Mag. 4, 269 (1959).

¹⁰ M. H. L. Pryce, Suppl. Nuovo cimento. 6, 817 (1957).

¹¹ D. Palumbo, Nuovo cimento 7, 271 (1958).

¹² R. Sternheimer, Phys. Rev. 84, 244 (1951); 95, 736 (1954); 105, 158 (1957).

FIG. 2. Quadrupole splitting of Fe^{57} 14.4-keV γ radiation.

that the directions of polarization could be varied. The ferrous fluosilicate absorber was a single crystal, approximately a rectangle 2×7 mm and about 1 mm thick and contained Fe^{57} in natural isotopic abundance. It was held at 90°K in a cryostat C having thin Mylar windows. The c axis was determined by visual inspection and confirmed by examination with polarized light. The transmitted γ rays were detected by a 1-mm thick NaI crystal and the amplified scintillation pulses were selected by a single-channel pulse-height analyzer, sorted according to the sign of the source velocity and scaled and recorded on printing registers. The complete apparatus operated automatically, the micrometer advancing a preset number of thousandths of an inch after the carriage had executed a preset number of traversals.

METHOD AND RESULTS

The energy levels of a nucleus of spin I and quadrupole moment Q in an axially-symmetric electric field with gradient eq (defined by convention to be $+\partial^2 V/\partial z^2$) are given by the Hamiltonian

$$3\mathcal{C}_Q = \frac{e^2 Q q}{4I(2I-1)} [3m^2 - I(I+1)].$$

The ground state of the Fe^{57} nucleus with $I = \frac{1}{2}$ is unsplit, while the first excited state with $I = \frac{3}{2}$ is split into two doublets separated in energy by $|e^2 Q q|/2$. If $e^2 Q q$ is positive the lower doublet has $m = \pm \frac{1}{2}$, while if it is negative that with $m = \pm \frac{3}{2}$ lies lower. The Mössbauer absorption spectrum for unpolarized monoenergetic 14.4-keV radiation therefore consists of two lines. If the incident radiation is linearly polarized and the absorber is a single crystal, so that the electrostatic potential has the same axis of symmetry for all the nuclei, the in-

tensities of the lines will depend upon the relative directions of the polarization vector and the crystal axis. Radiation which excites the $m = \pm \frac{3}{2}$ level has $\Delta m = \pm 1$, and the absorption is greatest when the electric vector of the incident radiation is parallel to the axis, while that leading to the $m = \pm \frac{1}{2}$ level has $\Delta m = 0$ or ± 1 and has maximum absorption when the polarization is perpendicular to the axis. The calculated intensities of the absorption lines are shown for the two polarization directions in Fig. 2, where it has been assumed that the $m = \pm \frac{3}{2}$ doublet was lower. Measurement of the spectrum for polarized γ radiation leads to an identification of the levels and hence to the sign as well as the magnitude of $e^2 Q q$ and also (using the calculated value for q) of Q .

Polarized 14.4-keV radiation may be produced by magnetizing a source of Co^{57} in ferromagnetic iron.¹³ The emitted spectrum consists of six lines whose intensities and directions of polarization (relative to the magnetizing field) are shown in Fig. 3(a). In principle the Mössbauer spectrum for any one of these components is sufficient to determine the sign of the quadrupole coupling in the absorber, but in practice it is necessary to examine the whole spectrum in order to sort out complications due to overlapping lines. The predicted velocity spectrum (assuming that the $m = \pm \frac{3}{2}$ doublet lies lower) is shown in Fig. 3(c) for magnetiza-

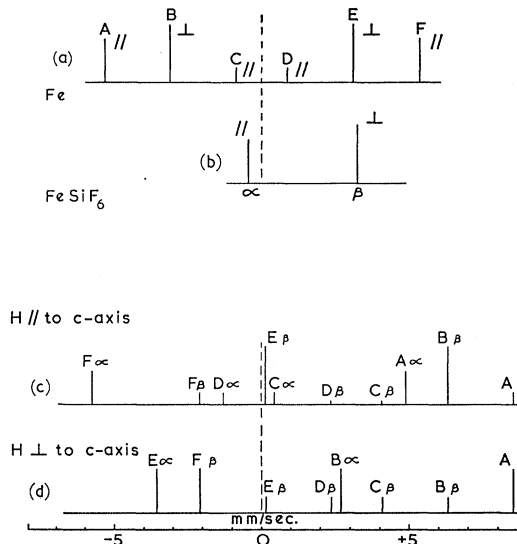


FIG. 3. (a) Emission spectrum of 14.4-keV radiation from Co^{57} in magnetized iron, showing \parallel (parallel) and \perp (perpendicular) polarizations with respect to the magnetization. (b) Absorption spectrum for 14.4-keV radiation of $\text{Fe}^{57}\text{SiF}_6 \cdot 6\text{H}_2\text{O}$. (c) Predicted Mössbauer spectrum of a single crystal of $\text{Fe}^{57}\text{SiF}_6 \cdot 6\text{H}_2\text{O}$ for 14.4-keV radiation emitted from Co^{57} in iron magnetized parallel to the crystal axis. The lines are identified by an upper case letter for the emitter and a Greek letter for the absorber. (d) Predicted Mössbauer spectrum: emitter magnetized perpendicular to the axis of the absorber.

¹³ G. J. Perlow, S. S. Hanna, M. Hamermesh, C. Littlejohn, D. H. Vincent, R. H. Preston, and J. Heberle, *Phys. Rev. Letters* **4**, 74 (1960).

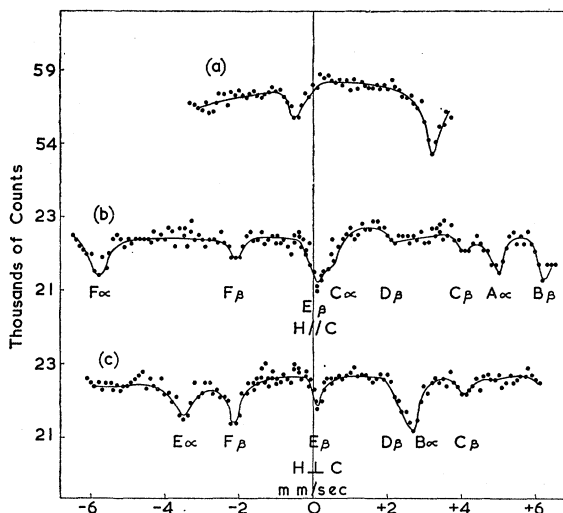


FIG. 4. Observed Mössbauer spectra for a single crystal of Fe⁵⁷SiF₆·6H₂O for 14.4-keV radiation emitted from (a) Co⁵⁷ in copper, (b) Co⁵⁷ in iron magnetized parallel to the crystal axis, and (c) Co⁵⁷ in iron magnetized perpendicular to the crystal axis. The lines are identified by comparison with Fig. 3.

tion parallel to the crystal axis and in Fig. 3(d) for perpendicular magnetization.

Figure 4(a) shows the spectrum of ferrous fluosilicate at 90°K for the monoenergetic unpolarized source in copper. The separation of the two lines is 3.70 ± 0.04 mm/sec, i.e., 43.0 Mc/sec, so $(e^2Qq)/h = 86.0$ Mc/sec. The spectrum was also measured at 77°K and 4°K and the same splitting was observed; at room temperature (290°K) the splitting was 3.5 mm/sec. The chemical shift of 1.40 ± 0.04 mm/sec with respect to metallic iron is close to that observed for many other Fe⁺⁺ salts.⁷

The measured spectrum obtained with a source of Co⁵⁷ in iron magnetized parallel to and perpendicular to the axis of the ferrous fluosilicate crystal are shown in Figs. 4(b) and (c), respectively. The spectra agree closely with those predicted in Figs. 3(c) and (d) and establish that the lowest level in ferrous fluosilicate has $m = \pm \frac{3}{2}$. The electric quadrupole coupling therefore has negative sign, i.e.,

$$(e^2Qq)/h = -86.0 \text{ Mc/sec.}$$

It may be noted that the intensity ratio of the two absorption lines for unpolarized radiation [Fig. 4(a)] is entirely consistent with the negative sign of the coupling. Adding the intensities for the two polarizations in Fig. 2, the absorption to the excited $m = \pm \frac{1}{2}$ state is seen to be favored by the factor 10:6 for radiation incident at 90° to the *c* axis.

INTERPRETATION

The electric field gradient at nuclei in an ionic solid arises from charge distributions of lower than cubic symmetry which may be located either (a) externally or (b) internally to the ion under consideration. The latter

usually occurs when the orbital levels of a paramagnetic ion are split by the noncubic electric field. In calculating the field gradient it is necessary to estimate the shielding or antishielding produced by the response of the electrons on the ion to the charge asymmetry. (the Sternheimer factor¹²). Generally, this correction term is smaller when the field gradient arises internally rather than externally.

In ferrous fluosilicate the distortion from cubic symmetry is small and by performing a summation over the lattice the external contribution to the field gradient was shown to be small. We, therefore, consider the calculation of the electric field gradient produced internally by the ferrous ion.

The ⁵D ground state of the free Fe⁺⁺ ion is split by a cubic field into an orbital doublet and an orbital triplet, the latter lying lower. The trigonal distortion in ferrous fluosilicate further splits the lower triplet into a singlet with wave function ψ_0 and a doublet which is a mixture of states $\psi_{\pm 2}$ and $\psi_{\mp 1}$; the subscripts are components of orbital angular momentum along the trigonal axis. Susceptibility measurements by Jackson⁹ show that the singlet is the ground state and calculations by Pryce¹⁰ and by Palumbo¹¹ combined with these data show that it lies lowest by about 1200 cm⁻¹. This is consistent with our observation that the quadrupole splitting does not change between 4° and 90°K. Since the trigonal field splitting is so much larger than the spin-orbit splitting (for the free Fe⁺⁺ ion $\lambda = 100$ cm⁻¹) the latter can be neglected in calculating the electric field gradient.

The field gradient is the expectation value of $-\sum_i (3z_i^2 - r_i^2)/r_i^5$ over the ground-state wave function ψ_0 which transforms like Y_2^0 . It is readily shown that this can be replaced by the single term

$$q = -\langle Y_2^0 | (3z^2 - r^2)/r^5 | Y_2^0 \rangle \\ = -(4/7) \langle r^{-3} \rangle_{3d}.$$

Taking $\langle r^{-3} \rangle_{3d}$ to be $5.1 a_0^{-3}$,¹⁴ we find from our value of e^2Qq that $Q = +0.12 \pm 0.01$ barn.

This value for Q is in fairly good agreement with that deduced by Abragam and Boutron⁴ (+0.09 b) and by DeBenedetti, Lang, and Ingalls⁷ (about 0.1 b), but is only about one third of that deduced by Burns⁵ ($\cong +0.4$ b).

Our result is subject to error from two sources. Firstly, we have ignored the internal Sternheimer factor: Abragam and Boutron estimate that this calculation will decrease the field gradient by at most 25%, i.e., it could increase Q by up to 25%. Secondly, the free-ion value we have used for $\langle r^{-3} \rangle_{3d}$ may not be appropriate for Fe⁺⁺ in its crystalline environment.

There appears to be a small but real discrepancy between our result and that of Abragam and Boutron. We have considered if this could be due to an admixture

¹⁴ Calculated by Mlle. F. Boutron from the wave functions of R. E. Watson, quoted in reference 4.

by spin-orbit coupling of other states into the ground state of FeF_2 ; this would reduce the field gradient and increase their deduced value of Q . However the latest determination of $g_{||} = 2.25 \pm 0.05$ by Ohlmann and Tinkham¹⁵ from antiferromagnetic resonance leads to too small an admixture to be significant. The precise cause of the discrepancy therefore remains unknown, but we suggest that it is due to changes in the effective value of $\langle r^{-3} \rangle_{3d}$ and the internal Sternheimer factor due to the different crystal environment of the Fe^{++} ion in the two crystals. It seems likely, therefore, that the discrepancy of 25% between the results gives some measure of the uncertainty in the deduced value of Q from the two sources of error we mentioned above.

The much more serious difference between the mo-

¹⁵ R. C. Ohlmann and M. Tinkham, *Phys. Rev.* **123**, 425 (1961).

ment deduced from measurements on Fe^{++} salts (references 4, 7, and the present work) and on Fe^{3+} salts⁵ cannot be explained satisfactorily at present. Part of the discrepancy may stem from the neglect of the effect of covalent bonding in the ferric salts (Fe_2O_3 and YIG) in the calculation of the effective electric field gradient acting on the electrons of the Fe^{3+} ion.

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We are indebted to Professor B. Bleaney for pointing out to us the special advantages of ferrous fluosilicate. Miss Mavis Bowler kindly carried out the computation of the lattice contribution to the electric field gradient. The single crystal was grown by Dr. P. D. F. Shaw. We thank Dr. T. E. Cranshaw and M. S. Ridout for their cooperation.

Sign of the Li^8 Magnetic Moment*

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The sign of the magnetic dipole moment of Li^8 has been found experimentally to be positive, in agreement with theoretical expectation. Rates of transition among the Zeeman levels were compared for the two senses of circular polarization of a resonant rf field (1977 kc/sec in 3139 gauss). The short half-life (0.85 sec) of Li^8 required use of the polarized neutron-activation, beta-emission anisotropy detection, method previously applied to the measurement of the Li^8 nuclear g factor.

WE have found the magnetic dipole moment of Li^8 to be positive by an experiment which compared the transition rates (among Zeeman levels) produced by resonant rf fields of alternatively positive and negative circular polarization. The short (0.85 sec) half-life of Li^8 required use of the polarized neutron-activation, beta-emission, anisotropy-detection technique by which the nuclear g factor was measured.¹

The sign of a magnetic dipole moment is conventionally defined so that a rotating positive charge has a positive moment.² Taking the direction of a static magnetic field \mathbf{H}_0 as given by the Lorentz equation $\mathbf{F} = (e/c)(\mathbf{v} \times \mathbf{H}_0)$, an observer looking in the field direction would see the Larmor precession of a positive moment as counterclockwise.³ It is well known that transitions among the Zeeman levels in a strong field \mathbf{H}_0 may be produced by a small perturbing field \mathbf{H}_1 which rotates synchronously with the Larmor precession. The

opposite sense of rotation is less effective⁴ by the factor $(H_1/H_0)^2$, usually of order 10^{-6} or less. Comparison of

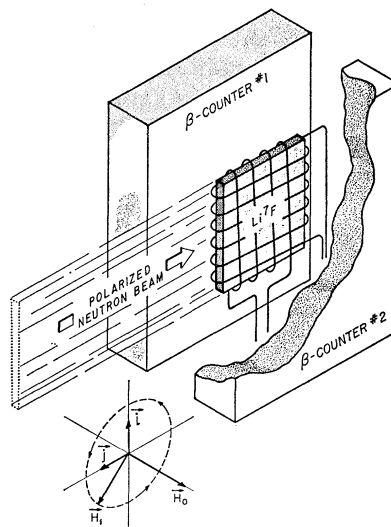


FIG. 1. Experimental geometry. Neutron and nuclear polarization are parallel to \mathbf{H}_0 . \mathbf{H}_1 rotates at the Larmor frequency in the $i-j$ plane, normal to \mathbf{H}_0 .

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

¹ D. Connor, *Phys. Rev. Letters* **3**, 429 (1959); Argonne National Laboratory Report ANL-6263, 1960 (unpublished).

² H. H. Staub and E. H. Rogers, *Helv. Phys. Acta* **23**, 63 (1950).

³ We apologetically use the symbol H for magnetic fields, following the nearly universal custom in the magnetic resonance literature.

⁴ F. Bloch and A. Siegert, *Phys. Rev.* **57**, 522 (1940).