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Quadrupole Coupling Constant, eqQ/h, of Fe^{3+} in Several Rare-Earth Iron Garnets

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Using the Mössbauer effect, values of eqQ/h of Fe^{3+} have been obtained at each of two sites in several rare-earth iron garnets. The measured values of eqQ/h were compared with values obtained using a point-charge lattice sum calculation. For the octahedral (a) site there was reasonable agreement between the measured and calculated values of eqQ/h indicating that an ionic model is reasonably valid. However, the measured values of eqQ/h at tetrahedral (d) sites were larger than those estimated. This difference is attributed to a small amount of covalent bonding which is also evident in the values of the (d) site internal field and isomer shift.

CONSIDERABLE interest has developed in recent years in estimates of crystal field potentials. For ionic crystals, lattice sum calculations using a point-charge model[1] have met with some success in estimating the field gradient q of interest in nuclear quadrupole resonance and for the calculations of the other crystal potentials[2] associated with the fitting of optical spectra of rare-earth ions. In the case of the calculations of the field gradient, the restricted success has arisen, in part, from the limited accuracy of the x-ray data used in the calculations and, in part, from the covalent-bonding effects at the ion in question.

The garnets represent a group of isomorphous compounds on which extensive x-ray measurements have been made.[3–5] Moreover, their magnetic properties have received considerable attention[6,7] and are well understood. With this in mind, we have measured the nuclear quadrupole coupling constant, eQq/h, of Fe^{3+} in several rare-earth iron garnets. The measured results were compared to a simple point-charge lattice sum calculation in the rare-earth ion garnets. This was done by comparing calculated values of the nuclear quadrupole-coupling constant, eqQ/h, for each of the two iron sites in the garnet structure with values of eqQ/h measured in a Mössbauer absorption experiment.

The rare-earth iron garnets [$R_3Fe_2(FeO_4)_3$, (RIG), where R is yttrium or a rare-earth ion] are ferrimagnetic to about 300°C. The garnets are cubic, of the space group O_h^{10}-$Ia3d$, with 160 atoms per unit cell.[8] There are 24 (d) sites where the Fe atoms see tetrahedral $\bar{4}$ symmetry and 16 (a) sites where the Fe atoms see octrahedral $\bar{6}$ symmetry. Recently, Alff and Wertheim[9] measured the value of eqQ/h of Fe^{3+} at the two sites of YIG at room temperature. This was done by observing the asymmetry of the nuclear hyperfine splitting in a single crystal for which the internal magnetic field had a definite orientation with respect to the principal axis of the q tensor. A thin single crystal of YIG was used as an absorber and a small external field served to orient the internal field along the proper crystallographic direction. Our measurements were made on six garnets above the Curie temperature. Thus, no magnetic field was present and single-crystal absorbers were unnecessary.

Most of the garnets were grown by E. A. Giess using published techniques.[10] One, LuIG, was prepared by firing the oxide in air at 1400°C for several hours. x-ray analysis verified the compositions of the various compounds. The resonant absorption spectra were obtained using a Co^{57} source diffused into copper. An absorber

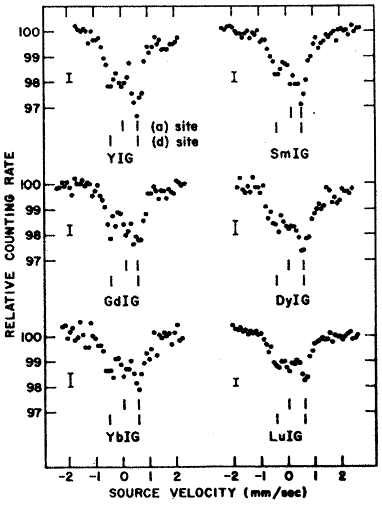

FIG. 1. Mössbauer absorption spectra of Fe^{3+} at two sites in several rare-earth iron garnets.

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consisted of a finely ground sample of a garnet placed in a heater assembly, the temperature of which was continuously monitored using a thermocouple in direct contact with the sample. A loudspeaker velocity drive was used in conjunction with a multichannel analyzer to obtain the absorption spectra. Calibration spectra were provided by a natural iron foil.

The observed absorption spectra are shown in Fig. 1 along with assigned quadrupole splittings. The assignment of absorption peaks to either the tetrahedral (d) sites or octahedral (a) sites is made using intensity data, the abundance of (d) to (a) sites being 3:2. Moreover, the isomer shifts measured here are consistent with those observed in the ferrimagnetic state by Wertheim[11] for the two sites of YIG (0.57 mm/sec and 0.26 mm/sec).

Values of q were calculated for each iron site assuming that all iron atoms were in a 3+ valence state. In this case q simply arises from the field of the neighboring ions. Hence,

$$q=(1-\gamma_\infty)q_u=(1-\gamma_\infty)\sum\frac{(3\cos^2\theta_i-1)}{R_i^3}e_i, \qquad (1)$$

where γ_∞ is the Sternheimer antishielding factor,[12] 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, and e_i is the charge of the ith ion; the sum is taken over all ions in the lattice except the one at $R=0$. The lattice sum was calculated on an IBM-7090. With one exception, the results from the x-ray data of Euler and Bruce[4] were used. The data of Weidenborner[5] were used in the case of GdIG. The results from the other x-ray data[3] are in good agreement. The value of γ_∞ for Fe^{3+} has been calculated by several authors.[13,14] The more recent[14] value $\gamma_\infty=-9.14$ is used here. The lattice sum, Eq. (1), need only be performed for the oxygen ions since one can use previous results[15] to obtain the contributions to q from the other ions. This is because the positions of the other ions are fixed by the space group and the contributions to q at the (d) and (a) sites are the same for all garnets except for a scale factor, the lattice constant cubed.

The measured values of eqQ/h and the isomer shift along with the calculated estimates of eqQ/h for the two sites are listed in Table I. A correction of 0.22 mm/sec has been applied to the isomer shift data to take into account the temperature dependence of the second-order Doppler effect (the measurements reported here were taken at temperatures between 600 and 620°K). By now there are quite a few estimates[15–20] of Q for the first nuclear excited state of Fe^{57}. Positive values are obtained from the 2+ ionic state[17–19] where the $3d^6$ electron configuration contributes most of the effect and from the 3+ ionic state[15] where lattice contribution is most important. A value of $Q=+0.2\times10^{-24}$ cm^2 was used to calculate the values of eqQ/h listed in Table I.

TABLE I. The calculated values of the quadrupole coupling constant eqQ/h, and measured values of eqQ/h and the isomer shift for the octahedral and tetrahedral sites of Fe^{3+} in several rare-earth iron garnets.

	Calculated		Measured values		Isomer shift[c] at 300°K with respect to stainless steel (mm/sec)
Garnet	q_u[a] (10^{14} esu/cm^3)	eqQ/h[b] (Mc/sec)	Observed splitting (mm/sec)	eqQ/h at 610°K (Mc/sec)	
Octahedral (a) sites					
YIG	−1.19	−17	0.52±0.04	12.1±0.9	0.49±0.04
SmIG	−0.91	−13	0.34±0.04	7.8±0.9	0.54±0.04
GdIG	−1.27	−19	0.38±0.08	8.8±1.9	0.55±0.08
DyIG	−1.25	−18	0.49±0.08	11.4±1.9	0.51±0.08
YbIG	−1.43	−21	0.50±0.07	11.6±1.6	0.53±0.07
LuIG	−1.81	−27	0.57±0.04	13.2±0.9	0.52±0.04
Tetrahedral (d) sites					
YIG	−0.47	− 7	0.92±0.04	21.3±0.9	0.32±0.04
SmIG	−0.43	− 6	0.83±0.04	19.3±0.9	0.29±0.04
GdIG	−0.33	− 5	0.89±0.08	20.6±1.9	0.29±0.08
DyIG	−0.67	−10	0.90±0.08	20.9±1.9	0.29±0.08
YbIG	−0.56	− 8	0.99±0.05	22.9±1.2	0.28±0.05
LuIG	−0.87	−13	0.95±0.03	22.0±0.7	0.33±0.03

[a] The x-ray data of Weidenborner (Ref. 5) were used to estimate q_u of GdIG. The data of Euler and Bruce (Ref. 4) were used for the remaining garnets.

[b] A value of (Ref. 14) γ_∞ of −9.14 and a value of Q of 0.2×10^{-24} cm^2 was used to calculate eqQ/h.

[c] A correction of +0.22 was applied to the isomer shift data observed at 610°K to obtain the room temperature values listed here.

It can be seen that there is remarkably little dependence of the observed values of eqQ/h on species, particularly for the tetrahedral site. The agreement between experiment and calculation for the (a) sites is good considering the approximate nature of the point charge lattice sum. For example, the effect of an induced dipole moment on O^{2-} is neglected. The dependence of eqQ/h of the (a) sites on species is also reproduced quite well in the calculations.

While the variation of eqQ/h of the (d) sites is qualitatively reproduced in the calculation, it is considerably greater than seen experimentally. Trouble might be expected for the tetrahedral (d) sites since there is strong evidence from the earlier Mössbauer isomer-shift measurements and from measurements of the internal magnetic field that the (d) site has more covalent bonding. This follows from the low value of the (d) site isomer shift (0.30 mm/sec versus 0.50 mm/sec or larger[11] for more ionic compounds) and the lower value of the internal field at 0°K [470 kG for the (d) site versus

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550 kG for an (*a*) site[21] and 660 kG for Fe^{3+} in[22] FeF_3].

Good agreement exists between our experimental value for eqQ/h of the YIG tetrahedral site and the value obtained by Alff and Wertheim.[9] However, eqQ/h for the octahedral site measured here is 45% lower. We attribute the difference to the unusual difficulty of measuring eqQ/h in the magnetic state at room temperature. In the geometry for which simple Mössbauer absorption spectra can be obtained the octahedral spectrum is particularly insensitive to the value of eqQ/h. We have theoretically investigated the possibility that the different values could arise from magnetostriction effects but find that such effects change eqQ/h very little. To investigate the possibility that q is temperature-dependent, eqQ/h was measured above 700°K. The results were identical with those obtained at 600°K.

In considering the various data for the (*d*) site it is easy to blame "covalency" for the deviation of the q from that calculated using a point-charge model, for the lower value of the isomer shift, and for the smaller internal field. However, it is not easy to be explicit about the form it may take and the degree to which might exist. Within 1%, the (*d*) site has the full Fe^{3+} moment of 5 Bohr magnetons.[7] Hence, negligible *d*-wave function is involved in the covalent bond. Some 4*s*-like wave function is undoubtably present as indicated by the isomer-shift data and by the lower value of the internal field. However, the amount cannot be specified accurately as the (*d*) site charge distribution may be contracted relative to that of the (*a*) site [the (*d*) site Fe-O distance is 1.88 Å versus 2.00 Å for the (*a*) site]. As is known theoretically[23] and experimentally,[24] a contracted charge density will reduce the absolute magnitude of the internal field and also the magnitude of the isomer shift.[25] In order to explain the larger q that we observe, a small amount of 4*p* wave function must be present in the bond. However, because of the limited knowledge of the appropriate wave functions, a quantitative estimate would not be very meaningful.

For the octahedral site the observed values of eqQ/h are from 30 to 50% lower than those estimated from point-charge lattice sum calculations. With the exception of GdIG (for which older x-ray data were used for the calculated value of eqQ/h), the difference between the calculated and experimental values of eqQ/h increases uniformly for heavier rare-earth ions. This indicates the presence of some size effect. However, when considering the approximate nature of the simple ionic model used, these deviations are to be expected. It thus appears that a value of $Q=+0.2\times10^{-24}$ cm^2 is consistent with the octahedral site data. It also appears that one can do reasonably well in calculating the variation of q from sample to sample in the rare-earth ion garnets at least at the octahedral (*a*) sites. This is understandable since the data for the isomer shift and internal field indicate much smaller covalent effects for the octahedral sites.

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