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Interaction Between Fe^{57} and Its Crystalline Surroundings

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The quadrupole splittings of the Mössbauer absorption patterns of Fe^{57} in $FeSO_4 \cdot 7H_2O$, $FeCl_2 \cdot 4H_2O$, and $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ have been measured as a function of temperature. Low temperature limiting values of the splittings are found to be .350 cm/sec, .315 cm/sec, and .277 cm/sec (all ±.005 cm/sec) respectively. The temperature dependence is interpreted in terms of the temperature dependent occupation probabilities of the triplet states of the ferrous *d* electron. Characteristic temperatures of 800°, 1000°, and 380° respectively are assigned. A computation indicates that the antishielding factor for the field gradient caused by the ferrous *d* electron is $\gamma = .42$. The magnitude of the quadrupole moment of the excited state of Fe^{57} is estimated to be .18 barn.

A study of the 14.4Kev emission line of Fe^{57} through the Mössbauer effect has yielded, in addition to several nuclear constants, some significant contributions to the study of ferromagnetic materials and various iron salts.

Three types of interaction between the nucleus and its crystalline host have been studied, namely the hyperfine magnetic interaction[1] between the nuclear magnetic moment and the effective internal magnetic field, the nuclear isomer shift[2),3)], which results from the change in nuclear charge radius upon gamma emission, and the electric quadrupole interaction[4] between the excited Fe^{57} nucleus and the interal electric field gradient. We wish to report on a study of the latter interaction in ferrous salts, its temperature dependence, a calculation of the appropriate antishielding factor, and the value of the nuclear quadrupole moment.

The ferrous ion is a $3d^6$ configuration and its state is $^5D_4$ (i.e., a full *d* subshell of electrons of one spin plus a single electron of oppositely directed spin). The free ion has a net orbital angular momentum which is quenched in the solid, the appropriate wave functions in the solid being linear combinations of terms of the form Y_2^m. In a cubic environment the appropriate combinations are the triplet states xy/r^2, xz/r^2, and yz/r^2, and the doublet states x^2-y^2/r^2, and $2z^2-x^2-y^2/r^2$. When the ion under consideration is surrounded by an octahedron of negative ions, the triplet states, whose lobes avoid these charges, are of lower energy. In a cubic symmetry, the triplet states are degenerate and no field gradient will exist at the nucleus. Removal of the cubic symmetry removes this degeneracy and in the cases which have been studied appears to give rise to energy separations which are of the order of kT at room temperature. In the ferrous salts $FeSO_4 \cdot 7H_2O$, $FeCl_2 \cdot 4H_2O$, and $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ the low temperature quadrupole splittings are roughly equal in spite of the widely varying environment of the ferrous ion. For this reason we assume that the dominant contribution to the electric field gradient comes from the *d* electron of the ferrous ion, and consider the crystalline environment only through its effect in splitting the triplet states. If we make the reasonable assumption that the nuclear relaxation time is long compared to the transition times between states of the triplet, the effective field gradient will be an average of the contributions of these three states, each weighted by the appropriate Boltzmann factor.

A spin 3/2 nucleus with quadrupole moment Q has, in an electric field, two energy levels with a separation

$$\Delta E = \frac{1}{2} e^2 qQ(1-\gamma)(1+(1/3)\eta^2)^{1/2} ,$$

where γ is the antishielding factor, $q = V_{zz}$ is the maximum principal field gradient, and $\eta = (V_{xx} - V_{yy})/V_{zz}$ is the asymmetry parameter. The occupation of a single state of the triplet gives $q = -(4/7)\langle r^{-3} \rangle$ and $\eta = 0$. If the occupation probabilities of the triplet states are

$\alpha^2, \beta^2, \delta^2$, we have

$$q=[-(4/7)\alpha^2+(2/7)(\beta^2+\delta^2)]\langle r^{-3}\rangle\ ,$$
$$q\eta=(6/7)(\delta^2-\beta^2)\langle r^{-3}\rangle\ ,$$
$$\varDelta E=(2/7)e^2Q(1-\gamma)(\alpha^4+\beta^4+\delta^4-\alpha^2\beta^2-\beta^2\delta^2-\delta^2\alpha^2)^{1/2}\langle r^{-3}\rangle\ .$$

If the triplet states have energies E_0, E_0+kT_1, and E_0+kT_2, insertion of the Boltzmann factors yields

$$\varDelta E=(2/7)e^2Q(1-\gamma)\frac{[1+e^{-2T_1/T}+e^{-2T_2/T}-e^{-T_1/T}-e^{-T_1/T-T_2/T}-e^{-T_2/T}]^{1/2}\langle r^{-3}\rangle}{1+e^{-T_1/T}+e^{-T_2/T}}=f(T_1, T_2)\ .$$

The measured quadrupole splittings are shown in Table I and in Fig. 1 the functions $f(T_1, T_2)$ are fitted to the experimental results. The data are not sufficiently accurate and extensive to yield accurate values of both T_1 and T_2. It was found that the $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$ data could be well approximated by choosing $T_2=2T_1$. In determining the parameters for the other two materials this relation was arbitrarily retained in order to provide a consistent means of assigning characteristic temperatures to the materials.

As would be expected, in ferrous ammonium sulphate with the ferrous ion in surroundings which deviate slightly from octahedral symmetry, a low characteristic temperature is observed. In ferrous chloride, with high anisotropy, a high characteristic temperature is observed. The differences of the low temperature limiting values of the quadrupole splittings result from the direct effects of the crystalline field which have been neglected here.

Table I.

	300°	195°	112°	77°
$FeSO_4\cdot 7H_2O$	.321	.337	.351	.350
$FeCl_2\cdot 4H_2O$	.300	.313	.312	.315
$Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$	.173	.224	.264	.274

All values are in cm/sec± .005 cm/sec.

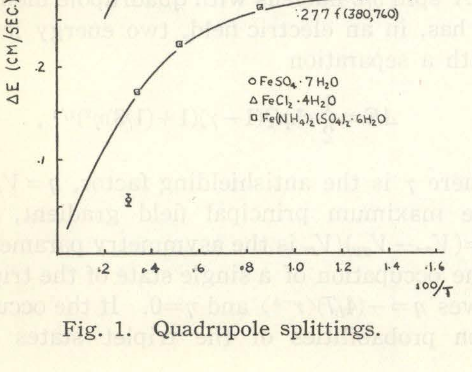

Fig. 1. Quadrupole splittings.

In the approximation that the low temperature splitting is attributable to the action of the ferrous d electron in a single one of its triplet states, it is possible to calculate the local field gradient and determine the nuclear quadrupole moment, provided that the appropriate antishielding factor is known. Mr. Robert Ingalls of our group has calculated the antishielding factor using the wave functions of Watson[5]. The resulting value is $\gamma=.42$. The nuclear quadrupole moment is then given by

$$Q=\frac{2\varDelta E}{(1-\gamma)qe^2}=.18\text{ barn}$$

where

$$\varDelta E=\frac{.31\text{ cm/sec}}{c}E_\gamma=1.10\times10^{-8}\text{ Rydberg}\ ,$$
$$1-\gamma=.58\ ,$$
$$q=(4/7)\times\langle 1/r^3\rangle_{3d}=(4/7)\times5.1/a_0{}^3\ .$$

The value of $\varDelta E$ in the above calculation is an average of the three observed low temperature limiting values, and $\langle r^{-3}\rangle_{3d}$ is the free ion value computed from the tables of Watson.

References

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DISCUSSION

W. **Marshall**: At Harwell, C. Johnson and G. Perlow have observed the quadrupole effect in $FeSiF_6 \cdot 6H_2O$ following a suggestion by B. Bleaney that the electronic structure of this compound is simple enough for the quadrupole moment to be deduced unambiguously. In this compound the orbital triplet is split by a large amount so that only the lowest state, an orbital singlet, is occupied. We deduce $(1-\gamma)Q=0.12$ barns, so if we accept your value for γ we deduce $Q \simeq 0.2$ barns in excellent agreement with your value of $Q=0.18$ barns.

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Mössbauer Study of $FeTiO_3$ and Its Solid Solutions with αFe_2O_3

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The solid solutions $(1-x)FeTiO_3$-xFe_2O_3 exhibit strong ferrimagnetic moments for the compositions $x<0.6$, where the Fe and Ti ions are ordered in the alternate (111) layers. The anomaly revealed by the Mössbauer measurements is that the ferrimagnetic phase consists of ferrimagnetic clusters surrounded by paramagnetic media. The size of these clusters decreases with increasing temperature or increasing local concentration of Ti. The isomer shift of $FeTiO_3$ is 1.2 mm/sec at room temperature as expected for Fe^{2+}. At 20°K, the hyperfine field was found to be 70 koe, considerably smaller than the expected value for Fe^{2+}.

Extensive investigation has previously been carried out on the $FeTiO_3$-αFe_2O_3 system by magnetic[1)-3)] and neutron diffraction[4)] measurements. It was shown that the ordering of Fe and Ti, in composition on the $FeTiO_3$ side, results in strong ferrimagnetic moments though both the end members are antiferromagnetic. (See Fig. 1.) These solid solutions were re-examined by Mössbauer effect[5)] in Fe^{57}, which gives new information concerning the magnetic as well as chemical environment.

Both ilmenite, $FeTiO_3$, and hematite, αFe_2O_3, have the rhombohedral structure. αFe_2O_3 can be visualized as consisting of layers of Fe ions in the (111) planes with oxygen layers between them. The structure of $FeTiO_3$ can be derived from that of αFe_2O_3 by replacing every other layer of Fe ions by a layer of Ti ions. The neutron diffraction studies[6),4)] have shown that in both compounds the Fe spins are parallel within a given (111) plane and antiparallel between adjacent planes.

The Néel temperature of the solid solution system, $(1\text{-}x)FeTiO_3$-xFe_2O_3, increases almost

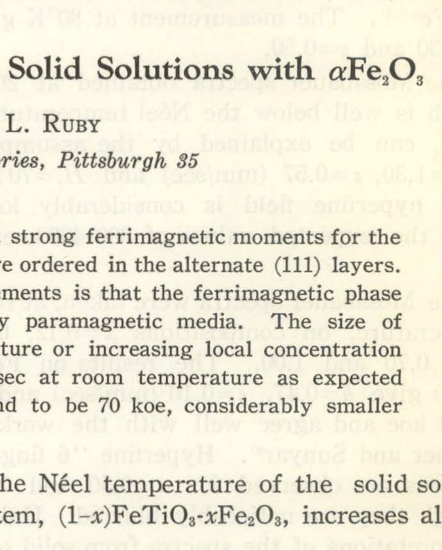

Fig. 1. Magnetic properties of $(1-x)FeTiO_3$-xFe_2O_3. According to Ishikawa and Akimoto[2)] and Bozorth, Walsh, and Williams[3)].