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HYPERFINE ANOMALY IN ^{193}Ir BY MÖSSBAUER EFFECT, AND ITS APPLICATION TO DETERMINATION OF THE ORBITAL PART OF HYPERFINE FIELDS*

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A 7% hyperfine anomaly is found in Mössbauer measurements of the 73-keV transition in ^{193}Ir. A 2% difference is found between the anomalies in antiferromagnetic IrF_6 and Ir-Fe alloy. The difference is ascribed to orbital contributions which differ for the two iridium environments. By using known details of IrF_6 we find the orbital field in the Ir-Fe to be $H_l = +335 \pm 200$ kOe.

We have observed a 7% hyperfine anomaly between the ground state and first excited state in ^{193}Ir by Mössbauer effect measurement, and a difference between the anomalies for iridium in ferromagnetic and antiferromagnetic environments. We are able to use the results to partition the hyperfine field at ^{193}Ir in an Ir-Fe alloy into a contribution due to a Fermi contact interaction and one due to noncontact fields, the latter being primarily orbital in origin. It is chiefly upon this new magnetic technique that we wish to report. The measurements of the anomaly will be treated briefly here and in detail in a later publication.[1]

Anomalous hyperfine interaction describes the difference between a nuclear magnetic moment measured in a uniform field and the moment measured in a magnetic field of hyperfine origin.[2,3] Since a hyperfine field is observable only in a product with a nuclear moment, the anomaly is observed by comparing the ratio of two moments or nuclear g factors measured in the two types of field. Many such anomalies between the ground states of a pair of isotopes have been measured, for example by atomic-beam techniques. Grodzins and Blum[4] made the first Mössbauer type measurement of the anomaly between two states of the same nucleus (the ground state and first excited state in ^{57}Fe), where it was found to be marginally small.

A large anomaly might be expected to be present in the iridium nuclei ^{191}Ir and ^{193}Ir.[5] The relatively large size of the nucleus results in a considerable variation of electron density over the nuclear radius. The contact hyperfine field, which depends on the density, is thus variable over the radius. The orbital and spin motions of the unpaired nucleons cause different radial distributions of magnetic moment and therefore contribute differently to the overall interaction in the radially varying density. The $\frac{3}{2}^+$ ground state of the odd-proton nucleus ^{193}Ir, for example, is favored for the effect because insofar as it is $d_{3/2}$ in character, the orbital and spin contributions to the nuclear moment tend to cancel, and a minor difference in the separate interactions shows up as a relatively large effect. The $\frac{1}{2}^+$ excited state at 73 keV is not so especially favored. It is the transition between these two states which we use.

We measured the ratio g^*/g^0 of excited-state to ground-state nuclear g factors in an external field of 73 kG supplied by a superconducting magnet. The absorber was iridium metal and the source ^{193}Os from neutron capture in ^{192}Os metal. The source itself has a small quadrupole splitting[6] which was taken into account in the fitting. The spectrum is incompletely resolved and contains two prominent outer lines and two weak inner ones. The separation of the prominent lines gives $g^* + g^0$. For g^0 we can take Narath's value[7] uncorrected for Knight shift and diamagnetism, namely $g^0 = +0.10589$. This is permissible since both measurements are done in external fields and on the same substance. With this we obtained $R_u \equiv g_u^*/g_u^0 = +9.51 \pm 0.03$. The subscript u indicates measurement with a field that is uniform over the nuclear volume.[8] This is to be compared with the same ratio measured in a 2.7-at.% alloy of Ir in Fe by Wagner et al.,[9] who obtained $R_{Fe} = +8.875 \pm 0.018$. As the measure of the anomaly we take

$$\Delta_{Fe} \equiv (R_u - R_{Fe})/R_{Fe} = 0.072 \pm 0.004. \quad (1)$$

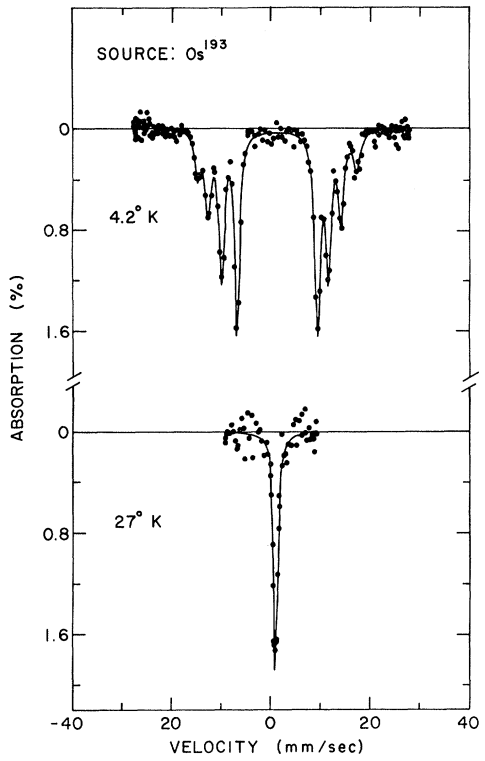

FIG. 1. Velocity spectrum of IrF_6 below and above the transition temperature.

The effect is thus quite large.[10]

Another series of measurements was performed with an absorber of IrF_6, an antiferromagnet with transition temperature at about 8°K.[11] We show two spectra in Fig. 1, one at 4.2°K and one at 27°K. There is indeed a magnetic transition lying between these temperatures. Table I gives some pertinent information from the fit. No constraints are applied. For the ratio of g factors, we find

$$R_{F_6} = \pm 9.045 \pm 0.039, \quad \Delta_{F_6} = 0.051 \pm 0.006, \qquad (2)$$

and

$$R_{F_6} - R_{Fe} = 0.170 \pm 0.043,$$
$$\Delta_{Fe} - \Delta_{F_6} = 0.021 \pm 0.007. \qquad (3)$$

It is a characteristic of such spectra that R, being dimensionless, is relatively insensitive to systematic uncertainties. We therefore believe the quoted error (which is due to statistics) to be realistic and the difference between the values of R (and of Δ) for the IrF_6 and alloy environments to be real. We ascribe the difference to a field which is uniform over the nucleus but different in the two magnetic samples.

Table I. Summary of IrF_6 results.

T (°K)	$\lvert H_n \rvert$ (kOe)	e^2qQ (mm/sec)	g^*/g^0	Isomer shift (mm/sec)
4.2	1850 ±6	−0.84 ±0.06	9.045 ±0.039	+0.89 ±0.02
27	~0			+0.91 ±0.02

Such a field can be obtained by (a) an orbital atomic moment μ_l which gives a contribution

$$H_l = 2\mu_l \langle r^{-3} \rangle_{av}, \qquad (4)$$

(b) a dipolar field H_d,[12] due to less than cubic symmetry of the spin distribution on the Ir. For this

$$H_d = \mu_s \langle 3\cos^2\theta - 1 \rangle_{av} \langle r^{-3} \rangle_{av} = \mu_B q,$$

where $qe = \partial^2 V/\partial Z^2$ and the symmetry axis Z is assumed to lie along the spin direction, and (c) Lorentz and other fields of remote dipoles in the ferromagnet. We neglect item (c) as small compared to the error in measurement. With the value $Q = +0.8$ b and the value of e^2qQ from Table I, we obtain $H_d = -16$ kOe, which is not important. Hence we ascribe the difference $R_{F_6} - R_{Fe}$ to a difference in orbital moment.

In order to assign numerical values to hyperfine fields, it is a great convenience to ascribe the anomaly to one state alone. From what has been said, the logical candidate is the $\frac{3}{2}^+$ ground state. Let the subscript c be assigned to any quantity measured in a field due only to Fermi contact interaction. Then $g_c^* = g_u^* = R_u g_u^0 = 1.007 \pm 0.003$, while $g_c^0 \neq g_u^0$. The total hyperfine field H_n can then be defined by the observed splitting in the excited state. It is readily shown that for iridium in chemical form A,

$$\Delta_A/\Delta_c = (H_c/H_n)_A, \qquad (5)$$

where

$$H_n = H_c + H_l + H_d + \cdots,$$

and $\Delta_A = (R_u - R_A)/R_A$ and $\Delta_c = (R_u - R_c)/R_c$. The quantity Δ_c is the anomaly for a pure contact field, a property of ^{193}Ir independent of chemical form.[13]

Our value $\Delta_{F_6} = 0.051$ provides a fair estimate for Δ_c. We think that a better value results from taking account of the small orbital component of electronic angular momentum in IrF_6. Spectroscopy of IrF_6 vapor and unpublished data on the crystalline solid as analyzed by ligand field theory lead to the description of the electronic ground state as predominantly $^4S_{3/2}'$ with small admix-

tures of $^2P_{3/2}'$ and $^2D_{3/2}'$.[14] The corresponding electronic magnetic moment then consists of an orbital part ($-0.114\mu_B$) and a spin part ($+2.77\mu_B$). The positive direction is taken as that of the total electronic moment. The spin moment results in the customary way in the contact field H_c, confidently predicted to be negative and hence in the same direction as the field H_l due to the orbital moment. Theoretical arguments lead to the expectation that the orbital contribution is not seriously quenched in the solid. The expectation is borne out by an analysis of Bromberg's data[11] on the magnetic susceptibility of IrF_6 between 13.9 and 300°K, which shows good agreement for the total atomic moment.

In order to calculate H_l from Eq. (4), we require the value of $\langle r^{-3}\rangle_{av}$. This was obtained from a Hartree-Fock calculation[15] in which we approximated the iridium electron configuration by (core)$5d^36s^26p$. The assumption is that the hexavalent Ir has in fact a charge of about +3. With this we found $\langle a_0^3/r^3\rangle_{av} = 14.1$. From all of this we can get H_l with an uncertainty of perhaps 20%. Then, neglecting H_d, we find for IrF_6 that

$$H_n = -1850 \pm 6 \text{ kOe}, \quad H_l = -200 \pm 40 \text{ kOe},$$

$$H_c = -1650 \pm 40 \text{ kOe}, \quad \Delta_c = 0.058 \pm 0.006.$$

We have determined experimentally that the field at the Ir nucleus in a dilute Ir-Fe alloy is negative. We can alter the value $|H_n| = 1495 \pm 15$ kOe quoted by Wagner et al. to conform to our convention on fields by multiplying it by $R_{Fe}/R_u = 0.933$. By the use of Eq. (5) and the value of Δ_c we can then decompose the field in the alloy and obtain

$$H_c/H_n = 1.24 \pm 0.15, \quad H_n = -1395 \pm 16 \text{ kOe},$$

$$H_l = +335 \pm 200 \text{ kOe}, \quad H_c = -1730 \pm 200 \text{ kOe}.$$

The orbital field has changed sign on going from the hexavalent Ir to the alloy. The contact fields are then found to be not substantially different. The sign change is consistent with the change from three electrons in the $5d$ shell to a comparable number of holes.

The accuracy of our result is not especially praiseworthy, but it can be appreciably improved in subsequent cases. There are a considerable number of the latter. The even-valence iridium ions form paramagnetic compounds to which, even if no convenient magnetic-ordering temperature exists, this method may be applied by causing splitting in external fields with $H/T \sim 10^4$ kOe/°K.

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