ELECTRIC QUADRUPOLE SPLITTING AND THE NUCLEAR VOLUME EFFECT IN THE IONS OF Fe^{57}†

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(Received December 19, 1960)

A study of the Mössbauer spectra of Fe^{57} in chemical compounds has revealed some striking regularities. Typical transmission curves for Fe^{++} and Fe^{+++} ionic compounds relative to an unsplit room-temperature stainless steel source are shown in Figs. 1 and 2, respectively. Both patterns exhibit a shift of the center of gravity from the zero of velocity, and the curve of Fe^{++} shows the two absorption lines characteristic of a pure nuclear electric quadrupole interaction. The quantities δ and ΔE, which characterize these effects, are defined in the figures; their values for various compounds are shown in Table I. It is noteworthy that the value of δ and the low-temperature value of ΔE are, for a given iron ion, relatively independent of the chemical combination.

The center of gravity displacement, or chemical shift,[1] arises from two mechanisms: (a) the second order Doppler shift,[2,3] which is caused by lattice vibrations, and is a function $A(T_s,T_a,\theta_s,\theta_a)$ of the source and absorber temperatures and Debye temperatures, and (b) the nuclear volume effect,[4,5] which represents the change, from source to absorber, in the modification of the nuclear transition energy caused by electrons overlapping the finite nucleus. The total shift in a Mössbauer spectrum may be written:

$$\delta \approx A(T_s, T_a, \theta_s, \theta_a) + B(R_e^{2\rho} - R_g^{2\rho})[\Psi_a^2(0) - \Psi_s^2(0)], \tag{1}$$

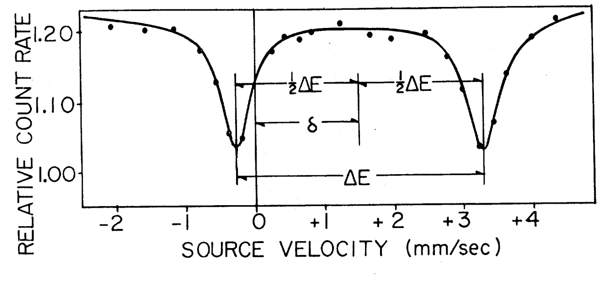

FIG. 1. Mössbauer spectrum of the Fe^{++} ion in an absorber of $FeSo_4 \cdot 7H_2O$ at nitrogen temperature using a room-temperature stainless steel source. The pattern exhibits the chemical shift δ and the electric quadrupole splitting ΔE of the excited state of the Fe^{57} nucleus. The velocity is positive for the source approaching the absorber.

where R_e and R_g are the charge radii of the nuclear excited and ground states. $\Psi^2(0)$ is the s-electron density at the position of the nucleus. B is a constant which is 1.76×10^9 cm/sec for iron when $R^{2\rho}$ and $\Psi^2(0)$ are expressed in atomic units. $\rho = (1 - \alpha^2 Z^2)^{1/2}$ is a relativistic factor[5] equal to 0.982 for iron.

An estimate of R_g/R_e may be made if one neglects the influence of the crystalline surroundings and uses wave functions[6] for the free iron ions. Using (1) and the room-temperature shifts (which are less sensitive to differences in θ than are the low-temperature shifts), we obtain

$$\delta_{++} - \delta_{+++} \approx B(R_e^{2\rho} - R_g^{2\rho})[\Psi_{++}^2(0) - \Psi_{+++}^2(0)]. \tag{2}$$

We have neglected the small difference $A_{++} - A_{+++}$. Watson's wave functions yield $\Psi_{++}^2(0) < \Psi_{+++}^2(0)$; the extra electron in Fe^{++} apparently shields the $3s$ electrons slightly. Equation (2) yields $R_g/R_e = 1.001$.

Watson[6,7] has also calculated wave functions for the outer electron configurations $3d^6 4s^2$ and $3d^8$ for iron. Using an equation similar to (2) one obtains the shifts expected for each case:

$$\delta_{Fe} = -0.178 \text{ cm/sec for } 3d^4 4s^2,$$

$$\delta_{Fe} = +0.182 \text{ cm/sec for } 3d^8.$$

When metallic iron is used as an absorber with the stainless steel source at room temperature, a shift of +0.01 cm/sec results. Since this value is midway between the above calculated values,

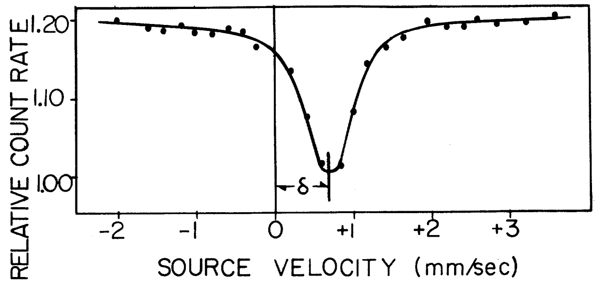

FIG. 2. Mössbauer spectrum of the Fe^{+++} ion in a $FeCl_3$ absorber at nitrogen temperature using a room-temperature stainless steel source. The velocity is positive for the source approaching the absorber.

Table I. A list of quadrupole splittings ΔE and chemical shifts δ relative to the emission line from a stainless steel source at room temperature.

Absorber	Temperature	ΔE(cm/sec)	δ(cm/sec)	References
Fe_2O_3	Room	0.024 ± 0.003	0.047 ± 0.003	a
Fe_2O_3	Room	0.024	0.050	b
$Fe_2(SO_4)_3$	Room	0	0.064	b
$Fe_2(SO_4)_3$	Room	0	0.055 ± 0.005	this work
$Fe_2(SO_4)_3$	Nitrogen	0	0.065 ± 0.005	this work
$FeCl_3$	Room	0	0.045 ± 0.005	this work
$FeCl_3$	Nitrogen	0	0.065 ± 0.005	this work
$FeCl_2 \cdot 4H_2O$	Room	0.300 ± 0.005	0.135 ± 0.005	this work
$FeCl_2 \cdot 4H_2O$	Nitrogen	0.310 ± 0.005	0.145 ± 0.005	this work
$FeSO_4 \cdot 7H_2O$	Room	0.320 ± 0.005	0.140 ± 0.005	this work
$FeSO_4 \cdot 7H_2O$	Nitrogen	0.360 ± 0.005	0.150 ± 0.005	this work
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	Room	0.175 ± 0.005	0.140 ± 0.005	this work
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	Nitrogen	0.270 ± 0.005	0.150 ± 0.005	this work
FeF_2	Room	0.268		c

[a] See reference 4.

[b] I. Solomon, Proceedings of the Allerton Park Conference on Mössbauer Effect, University of Illinois, Urbana, Illinois, June 5-7, 1960 (unpublished), Sec. IIc.

[c] G. K. Wertheim, Phys. Rev. 121, 63 (1961).

it strongly suggests that metallic iron has an outer electron configuration equivalent to $3d^7 4s^1$.

Although the electric quadrupole splitting seems to be temperature dependent, it is roughly the same at low temperatures for all the Fe^{++} compounds listed in Table I. This suggests that the relevant field gradient is mainly caused by the ion alone. The free Fe^{++} ion has an outer electron configuration of $3d^6$ and is in a ^5D state. Five of these $3d$ electrons have their spins aligned and together form a spherically symmetric distribution of charge. The sixth electron has opposite spin and also a choice of the five possible values of m_l. The crystal symmetry dictates the m_l combination the ion will actually take. For sufficiently low symmetry the lowest energy state will be a linear combination of the two states with m_l equal to 2 and -2. Assuming this, and neglecting all other possible effects of the crystalline environment, it is possible to calculate the ionic field gradient at the nucleus to within the factor $(1-\gamma)$, where γ is the Sternheimer antishielding factor. Taking ΔE to be 0.3 cm/sec one obtains $|Q(1-\gamma)| \approx 0.1$ b, where Q is the nuclear electric quadrupole moment for the excited state of Fe^{57}.

The temperature dependence of the quadrupole splitting could be caused by thermal excitation of the Fe^{++} ion into a state which yields a lower field gradient at the nucleus. For sufficiently rapid ionic transitions, the nucleus will respond to the time average of the field gradient. This interpretation indicates that the level splitting of the Fe^{++} ion in $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ is sufficiently small that significant excitation occurs at room temperature.

It is noted that there is very little quadrupole splitting in the case of Fe^{+++}. Presumably there is negligible field gradient from this ion, since its $3d^5$ electron configuration gives a ^6S state. The splitting that does occur[4] is therefore caused by field gradients from the neighboring ions rather than from the Fe^{+++} ion itself.

We are grateful to Professor J. Michael Radcliffe for some very helpful discussions.

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†This work was supported by the Office of Naval Research.

*Submitted by R. Ingalls in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology.

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[7] R. E. Watson, Phys. Rev. 119, 1934 (1960).

DETERMINATION OF THE PARITY CHANGE IN INELASTIC SCATTERING FROM THE ANGULAR DISTRIBUTION*

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Considerable success in determining the angular momentum transfer in direct-interaction inelastic scattering has been achieved by comparing the angular distribution in the approximate range 20° to 90° with $[j_L(KR)]^2$ or the improved theory due to Austern, Butler, and McManus.[1] Further information that one would like to obtain is the parity change of the nuclear state.

The distorted-wave Born approximation has been shown to give rather detailed fits to experimental data whether the final state is a single-particle[2] or collective[3] state. In a simplified distorted-wave Born approximation, Glendenning[4] found theoretical examples of angular distributions in which the forward differential cross section was very small for odd-parity change and very large for even-parity change. He suggested that this could be a general result which would make it possible to determine the parity change by a very simple experiment.

It is shown here in the distorted-wave Born approximation that, for reasonably small momentum transfers, the forward differential cross section is always small for odd-parity change and large for even-parity change. This result provides a very powerful tool for nuclear spectroscopy.

The matrix element for inelastic scattering in the distorted-wave Born approximation may be written

$$\mathfrak{M} \propto \int d^3r\, \varphi^{(+)}(\vec{\mathrm{k}},\vec{\mathrm{r}})\varphi^{(-)*}(\vec{\mathrm{k}}',\vec{\mathrm{r}})\Psi(\vec{\mathrm{r}}), \qquad (1)$$

where $\varphi^{(+)}$ and $\varphi^{(-)}$ are the wave functions of the incident and scattered particles whose momenta are $\hbar\vec{\mathrm{k}}$ and $\hbar\vec{\mathrm{k}}'$, respectively; $\Psi(\vec{\mathrm{r}})$ contains all the properties of the initial and final nuclear states and the interaction. In the case of single-particle excitations,

$$\Psi(\vec{\mathrm{r}}) = \int d^3r'\, \psi_i(\vec{\mathrm{r}}')v(\vec{\mathrm{r}},\vec{\mathrm{r}}')\psi_f^*(\vec{\mathrm{r}}'), \qquad (2)$$

where ψ_i and ψ_f are the initial and final single-particle wave functions.

In the case of rotational excitations by spinless particles, in the notation of reference 3,

$$\Psi(\mathrm{r}) \propto \sum_\mu \langle v_f | Y_L^{\mu}(\theta_1,\theta_2) | v_i \rangle Y_L^{\mu*}(\Omega)(dU/dr), \qquad (3)$$

where θ_1, θ_2 are the orientation angles of the nucleus with respect to the space-fixed frame; Ω is the angular part of $\vec{\mathrm{r}}$; v_f and v_i are the final and initial wave functions, respectively; and L is the orbital angular momentum change in the reaction.

The point is that the parity of $\Psi(\vec{\mathrm{r}})$ in all cases, whether the incident and scattered particles have spin or not, is determined by the parities of the initial and final nuclear states; that is the parity change of the nucleus.

The remaining factor in $\Psi(\vec{\mathrm{r}})$ has even parity including the pairs of spinor wave functions and spin-dependent interactions in the case where the scattered particles have spin.

The functions $\varphi^{(+)}$ and $\varphi^{(-)*}$ may be written

$$\varphi^{(+)}(\mathrm{r}) = \sum_l (2l+1)i^l \exp(i\sigma_l) R_l(kr)P_l(\cos\theta),$$

$$\varphi^{(-)*}(\mathrm{r}) = \sum_l (2l+1)(-i)^l \exp(i\sigma_l) R_l(k'r)P_l(\cos\theta'), \qquad (4)$$