V. CONCLUSIONS

(1) The theory for isomer shifts is essentially that for isotope shifts, and is well understood. Relativistic effects are very important in isomer shifts for heavy elements.

(2) Qualitative or semiquantitative chemical information, including the validity of "ionic character" in certain bonds, is readily available from isomer shifts. Relative values of $\Delta\psi^2(0)$ may be determined with high accuracy. Absolute values are unlikely to be obtainable to better than about 10% even in the most favorable cases and most cases will probably be considerably less accurate.

(3) Isomer shifts offer a useful method for obtaining conduction electron densities in metals. They should also prove very useful in studying bonding in intermetallic compounds.

(4) Derivation of the nuclear parameter $\delta R/R$ from isomer shifts can be quite useful in understanding nuclear structure, although great care must be taken in the interpretation. This parameter is most useful in cases where the level structure is already fairly well understood.

(5) Very large isomer shifts seem quite likely in the heavy rare earths and refractories. The large $\psi^2(0)$ from $6s$ electrons, the large relativity factors, and large and varying nuclear deformation combine to enhance the shifts here.

CONTRIBUTED PAPERS FOR SESSION I

Electric Quadrupole Splittings in Ferrous Compounds[*]

R. Ingalls,[†] *Carnegie Institute of Technology*

The various problems associated with interpretation of electric quadrupole splittings, obtained from Mössbauer experiments, are discussed. An attempt is made to express the electric field gradient tensor in ferrous compounds in terms of the d_ϵ energy splittings and the covalency factor, which roughly governs the values of $\langle r^{-3}\rangle$ and spin-orbit coupling constant, λ. In doing so, a detailed study of the problem, ferrous ion + ligands, is somewhat sidestepped. At the same time, however, one gains some insight concerning the behavior of the quadrupole splitting as a function of axial and rhombic crystalline field strengths and temperature. As a result of this study, one obtains an estimate of the quadrupole moment of Fe^{57m}, which agrees with that obtained from ferric Mössbauer experiments. Estimates, based upon Mössbauer results, are also made of the d_ϵ energy splittings in, $FeSiF_6 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, $FeC_2O_4 \cdot 2H_2O$, $Fe(NH_4SO_4)_2 \cdot 6H_2O$, $FeSO_4$, $FeCl_2 \cdot 4H_2O$, and FeF_2.

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[*] Supported by the Office of Naval Research and the National Science Foundation.

[†] Present address: University of Illinois, Urbana, Illinois.

Electric Field Gradient Measurements in Ferrous Compounds[*]

Peter Zory, *Carnegie Institute of Technology*

The nuclear electric field gradient (EFG) tensor parameters[1] in paramagnetic ferrous compounds may be adequately determined by transmitting monoenergetic, unpolarized Mössbauer radiation through "thin" single crystal absorbers. The EFG asymmetry N and the Euler angles connecting the EFG principal axes with the crystal axes are obtained from measurements of the orientation dependent ratio of the two absorption peak areas. The parameter q is then determined from the observed splitting. The analysis of $FeCl_2 \cdot 4H_2O$ is presented.

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[*] T. P. Das and E. L. Hahn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Suppl. 1.

[1] Supported by the Office of Naval Research and the National Science Foundation.

Determination of the Sign of the Electric Field Gradient in Randomly Oriented Samples

S. L. Ruby and P. A. Flinn, *Westinghouse Research Laboratories, Pittsburgh*

If single crystals are available, the determination of the sign and magnitude of the electric field gradient at Mössbauer nuclei is relatively straightforward. When the γ-ray direction is along the direction of the principal axis of the EFG tensor, then the intensity of the $\frac{3}{2}$ line is 3 times that of the $\frac{1}{2}$ line; in a perpendicular direction this ratio changes to 0.6. If only powdered crystals are available, and the direction of observation is therefore random with respect to the axis of the EFG, the amplitude of the two quadrupole peaks become equal (unless the thermal vibrations are markedly anisotropic) and other methods must be employed to determine the sign of q.

We have calculated the spectra resulting from the application of a magnetic field, both parallel and perpendicular to the γ-ray direction, to a randomly oriented sample with an axially symmetric EFG. We have chosen the size of the EFG to correspond to a total splitting (2ϵ) of 2.4 mm/sec; the magnetic field strengths are 16, 42, and 84 kOe. Our experimental linewidths have been folded into the computation.

The results indicate that the shapes of the two quadrupole peaks become distinguishable at less than 50 kOe applied field.

Mössbauer Study of Fe^{2+} in Ionic Crystals

Kazuo Ôno and Atsuko Ito, *University of Tokyo*

The data obtained in several ionic divalent iron crystals are listed in Table I. From obtained values of these parameters, we will discuss the ground states of Fe^{2+} in these crystals. It is noted that

(1) The ratio $q(FeSiF_6 \cdot 6H_2O)/q(FeCO_3)$ is $=1.8 \approx -2.0$. This confirms that the ground state of $FeSiF_6 \cdot 6H_2O$ is an orbital singlet (ψ_0), while that of $FeCO_3$ is an orbital doublet $(\frac{2}{3})^{\frac{1}{2}}\psi_{-2} + (\frac{1}{3})^{\frac{1}{2}}\psi_1$, $(\frac{2}{3})^{\frac{1}{2}}\psi_2 = (\frac{1}{3})^{\frac{1}{2}}\psi_{-1})$.

(2) Two forbidden lines were observed in $Fe_3(PO_4)_2 \cdot 8H_2O$ because of the existence of the large electric quadrupole interaction perpendicular to the internal magnetic field.

TABLE I

Substances	Temp.	$\frac{1}{2}e^2q$ (mm/sec)	Sign and direction[a] of principal q	δ mm/sec	H_i kOe
$Fe_3(PO_4)_2 8H_2O$	room	2.72		1.2	
	liquid N_2	3.08			
	liquid He		$q_x > 0$		296
	~1.8°K				300
$FeSO_4$	room	3.28		1.38	
	~15°K				split
	liquid He		$q_z > 0$		193
$Fe(CO_2)_2 2H_2O$	room	1.80			
	liquid N_2	2.13		1.30	
	liquid H_2	2.05			small
	liquid He		$q_x < 0$		174
$FeCO_3$	room	1.87		1.40	
	liquid N_2	2.12			
	liquid H_2	2.1	$q_z > 0$		170
$FeSiF_6 6H_2O$	room	3.56	$q < 0$[b]		
	liquid He	3.79			
$FeS_{1.00}$	room	0.32	$q_x < 0$[c]	0.80	308
Fe_3O_4	below 100°K	1.0	$q_z < 0$[d]	0.90	470

[a] Z is parallel to the internal field H_i, and $X_\perp H_i$.

[b] C. E. Johnson, W. Marohall, and G. J. Perlow, Phys. Rev. **126** 1503 (1962).

[c] K. Ôno, A. Ito, and E. Hirahara, J. Phys. Soc. Japan **17** 1615 (1962).

[d] A. Ito, K. Ôno, and Y. Ishikawa, J. Phys. Soc. Japan (to be published).

Quadrupole Splitting in Aurous Halides*

D. A. Shirley, R. W. Grant, and D. A. Keller, *Department of Chemistry and Lawrence Radiation Laboratory, University of California, Berkeley*

Using recoil-free absorption in Au^{197}, quadrupole splitting was observed in the aurous halides. Only a single line was found for several auric compounds. The isomer shifts, relative to a Au-in-Pt source, and quadrupole splittings were (in cm/sec): AuCl, −0.161 (20), 0.434 (40); AuBr, −0.143 (10), 0.410 (20); AuI, −0.124 (10), 0.383 (20); $AuCl_3$, +0.037 (15), 0; $KAuCl_4$, +0.036 (20), 0; $KAuBr_4$, +0.015 (15), 0. The quadrupole splittings in aurous compounds are consistent with linear sp hybrid x-Au-x bonds (estimating the field gradient for a $5p$ electron from that observed in Hg compounds and using the known quadrupole moment of Au^{197}). Square planar dsp^2 hybrid bonding in the auric halides should produce a similar splitting, but no splitting was observed.

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An Interpretation of the Mössbauer Spectra of Some Tin Compounds in Terms of the Valence State of the Tin Atom

M. Cordey-Hayes, *University of Birmingham, England*

The Mössbauer spectra of 20 inorganic compounds of tin have been studied. The isomeric chemical shift results are correlated with the electronic structures of the valence states of the tin atom and an estimate of the ionicities of the bonding orbitals made. In addition, a nuclear quadrupole interaction splits the absorption line into two components in many of the divalent compounds studied. Here the results are interpreted in terms of the p character and hybrid nature of the bonding and nonbonding orbitals.

Measurements have also been made with several organic tin compounds. By correlation with the inorganic compound data, the electronegativities of the organic groups have been estimated.

Chemical Shifts and Quadrupole Splittings in Iron Compounds

P. Remy and H. Pollak,* *Lovanium University, Leopoldville, Congo*

The chemical shift Δ is due to the interaction of the nuclear charge with the electron cloud. The electron density in the nucleus therefore depends on all neighborhood ions. When the surrounding ions are not in cubic sites, they produce an electric field gradient, which is studied in Mössbauer experiment by the quadrupole splitting ϵ.

Since chemical shifts and quadrupole splittings both depend on the neighbor ions, it may be expected that they are correlated.

A search for this correlation was undertaken in the case of iron compounds which have been widely and carefully studied by the Mössbauer tool.

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* On leave of absence of Centre d'Etudes de l'Energie Nucleaire (MOL, Belgium).

Study of Bonding in Iron Compounds via the Mössbauer Effect*

N. E. Erickson†, A. W. Fairhall, and J. G. Dash, *University of Washington, Seattle*

The Mössbauer effect, primarily through the chemical shift and quadrupole splitting of absorption lines, offers a new and sometimes unique method of investigating bonding in iron compounds. Several examples are given to show how Mössbauer spectra combined with more conventional measurements involving magnetic and optical properties of these same compounds can be used to unravel their bond characteristics. We would like to express our appreciation to R. M. Housley for many helpful discussions.

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† National Science Foundation predoctoral fellow.

A Convenient Sn^{119} Source

P. A. Flinn and S. L. Ruby, *Westinghouse Research Laboratories, Pittsburgh*

The usual tin sources are SnO_2 and white tin metal. Since both of these materials are noncubic, one expects the observed resonances to be somewhat broadened by quadrupole interactions. Most reported results with these sources indicate an observed line width of about 1 mm/sec, to be compared with a natural linewidth, based on lifetime measurements, of about 0.6 mm/sec.

We have investigated the intermetallic compound Mg_2Sn as a source. It provides a cubic environment for the Sn, has a moderately high melting point which indicates a stiff lattice, and the Mg atoms absorb a negligible amount of the Sn radiation. It can easily be prepared from liquid Sn and Mg vapor. Our experimental results indicate very nearly natural linewidth (full width at half-maximum is less than 0.70 mm/sec) and resonant fractions of approximately 0.3 at room temperature and 0.6 at 77°K.