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## MÖSSBAUER SPECTROSCOPY

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February 1971

### I. INTRODUCTION

It seems appropriate that Mössbauer Spectroscopy should be reviewed in a volume on magnetic resonance. These two fields overlap in many areas. They have several theoretical concepts and models in common, and they often play complementary roles in elucidating physical phenomena. Recently, for example, they have both been used intensively in studies of magnetic hyperfine fields and relaxation effects.

The question of whether Mössbauer Spectroscopy should be reviewed annually is another matter, one that certainly warrants discussion in the first such review. Consideration of this question has served to define the scope and format of this review: the arguments are given below.

Mössbauer spectroscopy is a large and diffuse field that spans several disciplines. Periodic bibliographies and reviews are especially important in

a field of this nature, in which it is impractical for each worker to keep abreast of the entire literature. The Mössbauer Effect Data Index (1) provides a complete, periodically revised, bibliography of the Mössbauer literature. Critical reviews in which a particular topic is discussed at length and in depth appear sporadically. This reviewer's interpretation of an annual survey is that it falls somewhere between these two extremes. Such a survey has the function of calling attention to a small number of topics of widespread interest on which progress is currently being made, and to give a short discussion of each topic. The survey will have fulfilled its purpose if it is useful in helping workers in Mössbauer spectroscopy keep up to date.

Because this survey has more the nature of a review than that of a compilation, and because of practical limitations on length, it was necessary to be highly selective in choosing topics for discussion. Emphasis is placed on topics that are fundamental to Mössbauer spectroscopy as a spectroscopic method, including studies in solid state physics. Applications in other areas, e.g. nuclear physics, chemistry, and biology, are not emphasized here. An outline is given below.

I. Introduction

Outline

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## II. SOURCES AND ABSORBERS

There have been several recent developments of general interest in this area.

### A. Zinc - 67

The 93-keV level of  $^{67}\text{Zn}$ , with a half-life  $T_{1/2} = 9.6 \mu\text{sec}$ , has tantalized Mössbauer spectroscopists for a decade. The quality factor  $E_Y/\Gamma_0 = 2.0 \times 10^{15}$ , which is about 600 times as large as that of the  $^{57}\text{Fe}$  resonance, gives  $^{67}\text{Zn}$  great potential for Mössbauer studies. The first unambiguous interpretation of a velocity spectrum has now been given by deWaard and Perlow (1), who used a piezoelectric velocity drive to obtain velocity spectra with sources of  $^{67}\text{Ga}$  in  $^{66}\text{ZnO}$  and absorbers of  $^{67}\text{ZnO}$ , both at liquid helium temperature. Their spectra, which ranged in velocity up to  $\pm 12$  microns/sec, showed a central line and several satellites. They obtained absorption effects up to 0.55% and linewidths in the range of 2.7 to 5 times the natural linewidth  $2\Gamma_0$ . They found a quadrupole coupling constant  $e^2qQ = 2.47 \pm 0.03 \text{ MHz}$  for the spin - 5/2 ground state of  $^{67}\text{Zn}$  in  $\text{ZnO}$ , and an asymmetry parameter  $\eta = 0.23 \pm 0.06$ . At a pressure of 40 kbar  $e^2qQ$  was reduced by 8%.



### B. Matrix Isolation of $^{57}\text{Fe}$

Barrett and McNab (2) have reported experiments on  $^{57}\text{Fe}$  atoms in a matrix of solid argon. To make this absorber an atomic beam of iron was produced and co-deposited with Ar on a beryllium disc at 4.2°K. They found two narrow peaks separated by  $4.06 \pm 0.03$  mm/sec as well as a broad absorption area. The two narrow peaks were interpreted as arising from  $\text{Fe}_2$  dimers. The possibility of obtaining spectra from single atoms by matrix-isolation studies is of considerable importance, as such spectra could provide reliable fiducial points based on atomic properties for isomer-shift and quadrupole splitting studies.

### C. $\text{Dy}^{4+}$ - a Single-Line Source

The rare earth series has long been a fruitful region for Mössbauer spectroscopy. The coincidence of a major region of nuclear deformation, which provides a plethora of low-energy nuclear transitions to ground states, and the rich hyperfine spectra made possible by the 4f electron configurations permits extensive application of Mössbauer spectroscopy to these elements. However, a lack of suitable sources renders these applications difficult. Khurgin,

Ofer, and Rakavy (3) have now made a narrow line source for the 25.6 keV resonance in  $^{161}\text{Dy}$ . This source consists of  $^{161}\text{Gd}$  in a  $\text{CeO}_2$  lattice. The  $^{161}\text{Gd}$  decays to form Dy in the +4 oxidation state, with configuration  $4f^8$ . The lowest crystal-field state is apparently a singlet, which would show no hyperfine structure. Presumably it is stated from the  $^7\text{F}$  manifold, perhaps the  $J = 6, M_J = 0$  state, which is well known in  $\text{Tb}^{3+} (4f^8)$ .

### III. INTERFERENCE BETWEEN MÖSSBAUER AND PHOTOELECTRIC ABSORPTION

#### A. E1 Transitions

In 1968 Sauer, Matthias, and Mössbauer (4) reported an asymmetric absorption line for  $^{181}\text{Ta}$ , which they analyzed as consisting of absorption and dispersion components. The latter was interpreted by Trammell and Hannon (5) and by Kagan, Afanas'ev, and Voitovetskii (6) as arising from interference between two processes. These processes are (a) Mössbauer absorption followed by electron conversion, and (b) atomic photoelectric absorption. Figure 1 shows the way in which the two processes are related, as well as a  $^{181}\text{Ta}$  spectrum (7). The total atomic cross section near the gamma resonant energy is given by (5)

$$\sigma = \frac{\sigma_0}{1 + x^2} (1 - 2\xi x) + \sigma_e ,$$

where  $x$  is the difference between the  $\gamma$  energy and the energy at resonance, in units of the experimental line width (half width at half maximum). Here  $\sigma_e$  is the atomic photoelectric cross section,  $\sigma_0(1 + x^2)^{-1}$  is the usual absorption component of a Mössbauer resonance line (including the Debye-Waller factor), and  $2 \xi x \sigma_0(1 + x^2)^{-1}$  is the interference term.

The interference parameter is given by (5)

$$\xi = \epsilon \left( \frac{\alpha \sigma_e'}{6\pi\lambda^2} \right)^{1/2},$$

where  $\alpha$  is the conversion coefficient,  $\sigma_e'$  is a partial cross section for photoelectric absorption, and  $\lambda$  is the  $\gamma$ -ray wavelength. The factor  $\epsilon$ , which could be somewhat less than unity, was introduced by Trammell and Hannon to account for the fact that  $\alpha$  and  $\sigma_e'$  are proportional to the sum of squares of transition amplitudes to various atomic final states, while  $\xi$  is proportional to the sum of products of these amplitudes. These authors showed that the dispersion parameter  $\xi$  will have the same value even if the experimental line-width exceeds the natural width because of inhomogeneous broadening or hyperfine interactions. They also indicated that  $\sigma_e \cong \sigma_e'$  to within a few percent.

Kaindl and Salomon (8) studied the  $^{181}\text{Ta}$  case further, showing that  $2\xi = 0.30 \pm 0.01$  for an unsplit line, in excellent agreement with the theoretical value  $2\xi = 0.31 \epsilon$ , if  $\epsilon \cong 1$ . This dispersion term is in very good agreement with the value  $2\xi = 0.32$  that can be derived from the spectrum of  $^{181}\text{Ta}$  reported by Sauer, et al. Kaindl and Salomon also fitted a magnetically-split

spectrum and a magnetic-drive spectrum with asymmetric lines, obtaining dispersion parameters  $2\xi = 0.30 \pm 0.01$  and  $2\xi = 0.35 \pm 0.07$ , respectively, for these two cases. The excellent agreement of the values of  $2\xi$  derived from the unsplit and magnetically-split spectra is in accord with the expectations of Trammell and Hannon.

While  $^{181}\text{Ta}$  gives by far the largest dispersion parameter, other El transitions also show the effect. Lukashevich, Gorobchenko, Sklyarevskii, and Filippov (9) found  $2\xi = 0.078 \pm 0.011$  for the 25.6-keV transition in  $^{161}\text{Dy}$  which compares well with a theoretical value  $2\xi = 0.077$ . By detecting conversion electrons they measured a related parameter, which we shall term  $\xi_e$ , related by

$$\xi_e = \left(\frac{1 + \alpha}{\alpha}\right) \xi$$

They found  $2\xi_e = 0.102 \pm 0.015$ , while theory (6) gives  $2\xi_e = 0.108$ . In another study, Henning, Baehre, and Kienle (10) reported  $2\xi = 0.07 \pm 0.01$  for this transition. These workers studied a total of five El transitions. Their results and those given above are collected in Table 1. An inspection of this table indicates that  $\epsilon \cong 1$  for every case.

B. M1 Transitions

Detection of gamma resonance-photoeffect interference by direct observation of asymmetry in absorption lines is feasible only for E1 transitions, but Afanas'ev and Kagan (11) predicted that similar interference effects for M1 transitions could be detected through a forward-backward asymmetry in the distribution of conversion electrons from the absorber. Mitrofanov, Plotnikova, Rokhlov, and Shpinel (12) have reported the observation of such an asymmetry in the 23.8-keV M1 resonance of  $^{119}\text{Sn}$ . Writing

$$\sigma = \frac{\sigma_0}{1 + x^2} (1 + \beta_{nl} x) + \sigma_e \quad ,$$

for an M1 transition, the interference parameter is given by

$$\beta_{nl} = d \cos \theta \quad ,$$

where  $\theta$  is the angle between the  $\gamma$ -quantum and electron momenta and  $d$  is a factor that depends on the electron subshell from which conversion takes place.

## IV. COLLECTIVE EFFECTS IN RESONANT NUCLEAR SCATTERING BY CRYSTALS

A. Theory

When a Mössbauer gamma quantum passes through a single crystal consisting in part of atoms of the resonant isotope, these atoms can interact collectively with the gamma quantum's wave field. When the Bragg condition is satisfied, under some conditions, the amplitudes for the formation of an excited state can have equal magnitude but opposite signs in the incident and diffracted waves. Because these waves are coherent, the formation probability for the excited state will vanish. In the simplest case, for example,  $\vec{k}$  or  $\vec{k}$  will have nodes at the nuclear sites. This results in a suppression of the inelastic channel corresponding to Mössbauer absorption, and the crystal becomes transparent when both the Bragg condition and the resonant Doppler velocity condition are satisfied. The effect can be observed either in transmission or in reflection.

Kagan and Afanas'ev predicted and discussed suppression of Mössbauer absorption in a series of theoretical papers (13-16). Kagan, Afanas'ev, and Perstnev (17) made a detailed analysis for the case of reflection. Recently

Pham Zuy Hien (18) has discussed the related question of spontaneous emission of  $\gamma$  quanta by a system of identical nuclei.

Apart from the problem of producing a suitable single crystal, two experimental difficulties must be dealt with in observing the collective effect. First, the angular dispersion of the  $\gamma$ -ray beam must be small, to satisfy the Bragg condition effectively. Second, the nuclear collective effect must be distinguished from the Borrmann effect (19-22), which is its atomic analogue.

In a paper on the theory of magnetic Mössbauer diffraction, Belyakov and Ajvazian (23) have discussed diffraction of Mössbauer radiation by magnetically ordered crystals containing resonant nuclei, in Born approximation. The Bragg and Rayleigh maxima don't coincide, and it should be possible to determine the orientation of the hyperfine field relative to the crystal axes.

B. Experiments on  $^{119}\text{Sn}$  and  $^{57}\text{Fe}$

A number of experimental observations of the nuclear collective effect have been reported recently. Voitovetskii, Korsunskii, and Pazhin (24) reported transmission and scattering measurements with the  $^{119}\text{Sn}$  resonance, using a single crystal of tin of natural isotopic composition. The collective effect was



observed in both cases, but the coherent resonant nuclear scattering amplitude,  $|f_n^r|$ , was smaller than the coherent electron scattering amplitude,  $f_e$ , so the Borrmann effect itself was very substantial in this early work. The two effects were distinguished by comparing spectra taken on and off resonance (the Borrmann effect is not a resonant process) and at different temperatures. The angular spread of the beam was 5'.

In later work on a tin single crystal enriched to 88% in  $^{119}\text{Sn}$ , Voitovetskii, et al. (25) found very large collective effects. Near resonance, where  $|f_n^r| > f_e$ , the absorption was substantially reduced at the Bragg angle. The velocity absorption spectrum was sharply asymmetric, as expected, because of interference between the (resonant) nuclear and (nonresonant) electronic scattering.

Sklyarevskii, et al. (26) studied the transmission of the 14.4-keV  $\gamma$  ray of  $^{57}\text{Fe}$  through a single crystal of (unenriched) iron with 3% silicon. These workers used a Ge crystal collimator to reduce the divergence of the incident beam to 7". They studied the angular dependence of the transmitted intensity near the Bragg angle  $\theta_B$  for source velocities ("on" and "off"

resonance),  $I_{\text{on}}(\theta)$  and  $I_{\text{off}}(\theta)$ . Both spectra showed pronounced Borrmann effects at  $\theta_B$ . Their ratio,  $I_{\text{on}}(\theta)/I_{\text{off}}(\theta)$ , in which the Borrmann effect is eliminated, showed a large nuclear effect, with the resonant absorption dropping from 23% for  $\theta \neq \theta_B$  to 5% for  $\theta = \theta_B$ .

Smirnov, Sklyarevskii, and Artem'ev (27) studied reflection of the 14.4-keV  $\gamma$  ray of  $^{57}\text{Fe}$  for the case  $|f_n^r| \gg f_e$ , using a crystal of  $\alpha\text{-Fe}_2\text{O}_3$  enriched to 85% in  $^{57}\text{Fe}$ . The line observed at the Bragg angle was asymmetric because of interference between electronic and nuclear scattering. The intensity of the diffracted  $\gamma$ -ray beam also showed evidence of an oscillatory dependence on Doppler velocity, which the authors also interpreted to an interference effect. Smirnov, et al. (28) also observed a broadened, non-Lorentzian line in Bragg reflection from this crystal, which they attributed to collective behavior.

Voitovetskii, et al. (29) studied tenth-order resonant Bragg scattering of 23.8-keV  $\gamma$  rays from tin single crystals enriched in  $^{119}\text{Sn}$ . In this case nuclear scattering was dominant ( $f_n^r/f_e = 150$  and  $50$  for the two beam polarizations), and they were able to obtain a diffracted (directed) beam of pure Mössbauer radiation.

## V. THE EVALUATION OF ISOMER SHIFTS

Kalvius (30) has given an up-to-date summary of the interpretation of isomer shifts. A few of the topics he has treated are discussed below.

Some common pitfalls in determining isomer shifts (second-order Doppler shifts, unresolved hyperfine structure) are described, and it is shown that  $\Delta \langle r^2 \rangle$  (not  $\Delta r/r$  or  $\Delta \langle r^2 \rangle / \langle r^2 \rangle$ ) is the nuclear quantity "measured" by isomer shifts, in the nonrelativistic limit. Relativity changes the exponent in  $\Delta \langle r^2 \rangle$  to a number less than 2. Using electronic wave functions obtained by solving the Dirac Equation in point nucleus approximation, one finds that  $\Delta \langle r^{2\sigma} \rangle$  is the appropriate moment, with  $\sigma = [1 - (Z\alpha)^2]^{1/2}$ , where  $Z$  is the atomic number and  $\alpha$  the fine-structure constant. Kalvius argues that expansion of the electron wave function within a finite nucleus in powers of  $r/R$ , where  $R$  is the nuclear radius, leads to the term  $\Delta \langle r^{2\sigma'} \rangle$ , with  $\sigma < \sigma' < 1$ . For  ${}_{93}\text{Np}$  he finds  $2\sigma' = 1.84$ , while  $2\sigma = 1.47$ . As  ${}_{93}\text{Np}$  is an extreme case (one of the heaviest elements), it follows that  $\langle r^2 \rangle$  is a good approximation in most cases.

Another interesting effect of relativity on isomer shifts is a great increase for heavy elements in  $\psi^2(0)$  of bound  $s$  electrons, when treated

relativistically, over the nonrelativistic result  $\Phi^2(0)$ . The relativity factor  $S'(Z) = \psi^2(0)/\Phi^2(0)$  was tabulated (31) earlier. Its validity has been questioned, but comparison of electronic wavefunctions obtained by direct calculations using the Dirac-Slater and Hartree-Fock-Slater methods (32) appeared to support the use of  $S'(Z)$ . More recent work on  ${}_{93}\text{Np}$  by Dunlap et al. (33), using SCF methods, also indicate that the tabulated  $S'(Z)$  is roughly correct (perhaps  $\sim 15\%$  high). These workers have also found that nonrelativistic calculations give the proper trends in electron density with the removal of various valence electrons, but that absolute values of  $\Delta\psi^2(0)$  and  $S'(93) \times \Delta[\Phi^2(0)]$  may differ by as much as 50%. At first this may seem surprising, but a little reflection shows that is is perhaps to be expected. The point is that relativistic and nonrelativistic electron configurations in heavy elements are difficult to compare, because the one-electron orbitals do not have the same orbital symmetry in the two cases. In the relativistic case  $\ell$  is not a good quantum number. Thus it is not surprising that a "p" electron, for example, shows different shielding effects in relativistic and nonrelativistic calculations.

One further effect of relativity deserves comment. The small component of a bound  $p_{1/2}$ -electron wave function is s-like: thus  $\psi_{np_{1/2}}^2(0)$  is

finite. In fact Kopfermann had estimated

$$\frac{\psi_{np_{1/2}}^2(0)}{\psi_{ns_{1/2}}^2(0)} \approx \alpha^2 Z^2 .$$

This ratio would be 0.46 for  ${}_{93}\text{Np}$ . In fact Dunlap et al. (33) find from SCF calculations that it is only about 0.1. For  ${}_{79}\text{Au}$  Faltens (34) had noted an even smaller ratio, as expected for this somewhat lighter element. Thus it appears that  $p_{1/2}$  electrons are less important than previously believed.

Kalvius has discussed at some length the relative merits of two methods for estimating one-electron contributions to  $\psi^2(0)$ . The first, and older, method is derived from atomic spectroscopy. It is based on the Fermi-Segrè-Goudsmit formula. The second method consists of using atomic self-consistent field calculations. The SCF approach is certainly preferable for determining properties of one-electron orbitals in atoms, and as SCF programs have become easily accessible, this method has almost completely replaced the FSG formula for this purpose. In Mössbauer spectroscopy, however, the question of whether SCF or FSG estimates are superior is really a fine point in comparison with the crudity of the approximation entailed when free-atom wave functions are

used to describe solid-state phenomena. Like many semiempirical approaches, the use of optical data in interpreting Mössbauer spectra may well give results that are quantitatively more accurate than the SCF approach, simply because the optical data contain empirical corrections for effects (e.g. configuration mixing) that the atomic SCF calculations do not consider explicitly. Thus the "solid-state factor",  $D_s$ , introduced by Hüfner and co-workers (35,36) may have empirical validity that would be difficult to reproduce from free-atom SCF theory, but its interpretation in terms of free-atom one-electron orbitals would be speculative.

Kalvius has also discussed briefly the attempts to improve estimates of  $\psi^2(0)$  by molecular-orbital calculations. One new approach has been given by Inglesfield (37), who considered the pseudopotential model for calculation of band structure as a method to obtain  $\psi^2(0)$ . He made a qualitative application (38) to  $^{119}\text{Sn}$  and was able to explain the relative isomer shifts in  $\alpha\text{-Sn}$ ,  $\beta\text{-Sn}$ , and  $\text{Mg}_2\text{Sn}$ . He found that changes in the "free-electron" density and in the band structure both affect  $\psi^2(0)$ , with the former dominating. The model could almost explain the decrease of  $\psi^2(0)$  in  $\beta\text{-Sn}$  on compression as arising from the band-structure term. Unfortunately the free-electron term was too large and had the

wrong sign (i.e., an increase in  $\psi^2(0)$ ). The pseudopotential model shows promise in explaining isomer shifts, but it is too early to tell how useful it will be.

The final conclusions given by Kalvius are rather discouraging. He has estimated that the absolute calibrations of isomer shifts are still uncertain by factors of  $\sim 3-5$  even for  $^{57}\text{Fe}$  and  $^{119}\text{Sn}$ , with  $\Delta \langle r^2 \rangle = -15 \pm 10 \text{ fm}^2$  for  $^{57}\text{Fe}$  and  $\Delta \langle r^2 \rangle = 6 \pm 3$  for  $^{119}\text{Sn}$ .

VI. NUCLEAR PARAMETERS:  $\Delta \langle r^2 \rangle$ 

In his review on isomer shifts Kalvius (30) has discussed the problems associated with extracting the nuclear parameter  $\Delta \langle r^2 \rangle$  from isomer-shift data. The paper includes an edited table of values of  $\Delta \langle r^2 \rangle$  obtained from 59 Mössbauer resonances in isotopes ranging from  $^{40}\text{K}$  to  $^{243}\text{Am}$ . The reader is referred to this review and table for an up-to-date discussion of the  $\Delta \langle r^2 \rangle$  parameter. A few of the highlights from this review and the 1970 literature are given below.

Rothberg, Guinard, and Benczer-Koller (39) have made a novel contribution to the determination of the nuclear factor for the  $^{119}\text{Sn}$  resonance. They studied the temperature dependence of the isomer shift in  $\beta\text{-Sn}$  and related it to the temperature dependence of the Knight shift. The position of the Mössbauer line at temperature  $T_a$ , written as  $\delta(T_a)$ , was given in terms of the position at  $77^\circ\text{K}$  as

$$\delta(T_a) = \delta(77) + \frac{3k}{2Mc}(77 - T_a) + \frac{3k\theta^2}{40Mc} \left( \frac{1}{77} - \frac{1}{T_a} \right) + \int_{77}^{T_a} \left[ \left( \frac{\partial \delta_{IS}}{\partial T} \right)_V + \left( \frac{\partial \delta_{QS}}{\partial T} \right)_V - \frac{\alpha}{\beta} \left( \frac{\partial \delta}{\partial P} \right)_T \right] dT$$



Here the second and third terms describe the second-order Doppler effect and the third term in the integrand represents the volume expansion effect ( $\alpha$  and  $\beta$  are the coefficients of expansion and compressibility respectively: the notation has been changed from that in Ref. (39)). After correction for these effects and that of quadrupole splitting, the authors obtained the relation

$$\left(\frac{\partial \delta_{IS}}{\partial T}\right)_V = 1.23 \times 10^3 \left(\frac{\delta R}{R}\right) \left(\frac{\partial \psi^2(0)}{\partial T}\right)_V .$$

Comparison of  $\left(\frac{\partial \psi^2(0)}{\partial T}\right)_V$  from the known temperature dependence of the Knight shift with this equation yielded a value

$$\left(\frac{\delta R}{R}\right) = +(1.8 \pm 0.4) \times 10^{-4} ,$$

for  $^{119}\text{Sn}$ . This value compares very well with the new result

$$\frac{\delta R}{R} = +(1.84 \pm 0.37) \times 10^{-4} ,$$

obtained by Emery and Perlman (40) from re-evaluation of their conversion-electron data. Analysis of the temperature-dependence, rather than the isomer shift itself, avoids a common objection to the comparison of Knight-shift and isomer-shift data, namely that the former measures  $\psi^2(0)$  evaluated only at the

Fermi energy while the latter samples  $\psi^2(0)$  throughout the band. In this case only electrons near the Fermi energy can participate in the temperature dependence of either parameter.

The question of polarization effects, in which the nuclear charge distribution is affected by the electronic charge distribution, is still not settled. For rotational nuclei Speth (41) reported a "linear polarization" effect which, however, Mang, Meyer, Speth, and Wild (42) proved to be identical to the usual isomer shift, within the self-consistent cranking model. The effect may be regarded either as lowering of the energies of the proton states through Coulomb shielding by electrons in the nucleus, giving a shift in the transition energy from the spin-I state to the (spin-zero) ground state in a rotational band of

$$\Delta E(I \rightarrow 0) = \lambda \frac{I(I+1)}{\theta_0^2} \Delta V$$

Here  $\theta_0$  is the equilibrium moment of inertia,  $\Delta V$  is the perturbing potential, and  $\lambda$  is a strength parameter that goes to 1 at the end of the calculation.

The alternative approach is to calculate the energy shift accompanying a linear

change in the moment of inertia incurred by the additional potential. This result is

$$E(I \rightarrow 0) = -\lambda \frac{I(I+1)}{2\theta_0} \frac{\Delta\theta}{\theta_0}$$

Mang et al. showed that  $2\Delta V = -\Delta\theta$ , thus demonstrating the equivalence of these two pictures. A simple explanation of this result is the following: if a system of one-particle states in a deformed potential  $V_0$  is subjected to an additional uniform potential  $\Delta V$  that lowers the energies of the single particle states, the system will accommodate by further deformation of  $V_0$ .

Kalvius (30) has discussed the  $\delta \langle r^2 \rangle$  results obtained to date in rotational nuclei, and their comparison with theory. He concludes that the agreement is reasonably good.

For spherical nuclei the situation is rather dismal. Agreement between experiment and theory is spotty at best. However, Kalvius has pointed out a very interesting regularity in  $\Delta \langle r^2 \rangle$  for transitions between  $2d_{5/2}$  and  $1g_{7/2}$  proton states. At the beginning and end of the  $1g_{7/2} - 2d_{5/2}$  subshell, the difference  $|\langle r^2 \rangle_{2d_{5/2}} - \langle r^2 \rangle_{1g_{7/2}}|$  is a maximum, for  $^{121}_{51}\text{Sb}$  and  $^{151}_{63}\text{Eu}$ , and

it drops to a minimum near the middle of the shell, in  $^{133}_{55}\text{Cs}$ , as shown in

Fig. 2. Kalvius (43) has also pointed out a similar regularity in the nuclear moment ratio for these two states. At present there is no theoretical explanation for this remarkable regularity, although it fairly cries out for one.

## VII. OTHER NUCLEAR PARAMETERS

Inspection of a new table of nuclear moments (44) shows that Mössbauer spectroscopy has been useful in the measurement of approximately 60 nuclear magnetic dipole moments and 30 electric quadrupole moments. In some cases the Mössbauer values have quite high precision, especially for cases in which moment ratios are measured. The technique has been very valuable in clarifying the experimental situation for rotational  $2+$  states in even-even rare-earth nuclei. The limitations of Mössbauer spectroscopy in moment studies is obvious. The good cases are gradually exhausted and experimenters are restricted to improving the accuracy of previously known values and extension to a few difficult new cases: The present situation may be described in this way.

Two "well-established" parameters have been recently challenged. Lejeune, et al. (45) have suggested, on the basis of both linewidth and delayed-coincidence studies, that the lifetime of the 23.8-keV level in  $^{119}\text{Sn}$  is 23 nsec rather than 18.4 nsec. D. P. Johnson (46) has remeasured the resonant cross section for  $^{57}\text{Fe}$ , finding a value  $\sigma = (2.56 \pm 0.05) \times 10^{-18} \text{ cm}^2$ , higher than the previously accepted result. This implies a conversion coefficient of

$8.19 \pm 0.18$ , which is lower than most earlier values. There are difficulties entailed in measuring both parameters ( $T_{1/2}$  for  $^{119}\text{Sn}$  and  $\sigma$  for  $^{57}\text{Fe}$ ), and this reviewer regards the true values of both as still being uncertain.

Ehnholm et al. (47) have used Mössbauer spectroscopy in  $^{197}\text{Au}$  to determine the ratio

$$\beta^2 = \frac{\text{Intensity of } L = 1 \text{ character}}{\text{Intensity of } L = 0 \text{ character}},$$

in the first-forbidden decay of oriented  $^{197}\text{Pt}$  nuclei. The angular momentum ( $L = 0$  or  $1$ ) carried off by the lepton system affects the relative populations of the magnetic substates in the upper (77 keV) level of the Mössbauer transition, and thus the relative intensities of the hyperfine components are altered. The same information can be obtained through  $\beta$ -asymmetry studies or  $\gamma$ -ray circular polarization measurements. These workers found  $\beta^2 = 7 \pm 1$  for the high-energy  $\beta$  branch in this decay.

## VIII. HYPERFINE ANOMALIES

If the magnetic hyperfine structure constants of two nuclear levels in the same atomic environment,  $a_1$  and  $a_2$ , are compared, their ratio is expected to be essentially that of the respective nuclear  $g$  factors. When the hyperfine interaction arises from Fermi contact interaction, however, this proportionality may no longer hold, and a hyperfine anomaly  ${}^1\Delta^2$ , given by the relation

$${}^1\Delta^2 = \frac{a_1 g_2}{a_2 g_1} - 1, \quad (48)$$

is said to exist. The origin of this effect was explained by Bohr and Weisskopf (48).

In a heavy atom the density  $\psi^2(r)$  of an electron in a bound  $s$  orbital decreases substantially between the center of the nucleus and the nuclear surface. A nucleon's magnetic  $g$  factor  $g_I$  may be partitioned into spin and orbital contributions  $g_s$  and  $g_l$ . The spin part interacts with the electron spin density at the instantaneous position of the nucleon, while the orbital part interacts with the average spin density through the orbit. Thus  $g_s$  and  $g_l$  experience different hyperfine magnetic fields in the contact interaction, and

the average field sensed by  $g_I$  varies depends on the nucleon distribution.

Both  $g_s$  and  $g_l$  are subject to smaller hyperfine fields in a real nucleus than they would find if the nucleus were a point dipole. This fact is usually noted by writing

$$a = a^0 (1 + \epsilon) ,$$

where  $a^0$  is the hyperfine constant that would be observed for a point nucleus.

The factor  $\epsilon$  is related to  $\Delta$  by

$$1/\Delta^2 = \frac{\epsilon_1 - \epsilon_2}{1 + \epsilon_2} \cong \epsilon_1 - \epsilon_2 .$$

The hyperfine anomaly is usually small (of the order  $10^{-2}$ ), but it can have any value, including infinity (49).

The determination of a hyperfine anomaly usually requires four measurements. Both  $g_1$  and  $g_2$  must be measured in a uniform (usually external) field, then  $a_1$  and  $a_2$  must be measured in a hyperfine field in which a contact term is present. If the fractional contribution of the contact term to  $a_1$  and  $a_2$  is known then the relative importance of  $g_s$  and  $g_l$  in the nuclear state may be determined, and conversely.



In Mössbauer spectra the experimental requirements are a little different. Determination of the anomaly between the excited and ground states of a resonant transition requires the measurement of only two spectra, because  $1/\Delta^2$  depends only on the ratios  $a_2/a_1$  and  $g_2/g_1$ . Thus Crecelius and Hufner (50) found an anomaly of 0.81% between the excited and ground state moments in the 22-keV transition in  $^{151}\text{Eu}$  by comparing hyperfine spectra in  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  absorbers. In  $\text{Eu}^{3+}$  ( $4f^6; ^7F_0$ ) the hyperfine magnetic field is almost entirely orbital in character, arising from admixtures of higher states, while in  $\text{Eu}^{2+}$  ( $4f^7; ^8S$ ) the field has contact character. The difference between the distributions of the contact and orbital hyperfine fields within the nucleus was sufficient to produce the observed anomaly.

Perlow and co-workers (51) found a large anomaly in the  $^{193}\text{Ir}$  resonance. Additional measurements were made by Wagner and Zahn (52). Perlow (53) has given a detailed discussion of hyperfine anomalies, especially as applied to the  $^{193}\text{Ir}$  case.

The resonance transition in  $^{193}\text{Ir}$  connects an excited  $1/2+$  state to the  $3/2+$  ground state. While the nuclear structure of the  $1/2+$  state is not well

established, it is probable that the anomaly is mostly attributable to the  $3/2^+$  state. The reason for this is simple. In any odd-proton state with  $j = l - 1/2$  ( $p_{1/2}$ ,  $d_{3/2}$ ,  $f_{5/2}$  ...) the spin and orbital contributions to the magnetic moment may each far exceed the value of the moment itself. Thus the effects of distributed nuclear magnetism are exaggerated. In the limiting case the resulting anomaly could be infinite (i.e., for  $g = 0$  but  $a \neq 0$ ) (49). In the  $3/2^+$  proton states studied thus far in Ir and Au isotopes, the observed anomalies are in the 5-10% range (53). While the sign and approximate magnitudes of the anomalies involving these  $3/2^+$  states may be understood as indicated above, in terms of the properties of a  $d_{3/2}$  proton state, quantitative agreement is not so easily attained. In fact Perlow has shown (53) that four nuclear models all predict anomalies for  $^{193}\text{Ir}$  that are much larger than that observed.

The  $^{193}\text{Ir}$  anomaly yielded a very interesting result. By analyzing three spectra, in an external field,  $\text{IrF}_6$ , and  $\text{IrFe}$ , Perlow et al. (51) obtained not only the anomaly itself but also the fractional orbital contribution to the hyperfine field at the Ir site in an  $\text{IrFe}$  alloy. They resolved the hyperfine field of  $-1395 \pm 16$  kOe into an orbital contribution of  $+335 \pm 200$  kOe and a

contact term of  $-1730 \pm 200$  kOe. Fox and Stone (54) found a similar result for Au in an Au Fe alloy, with the orbital contribution in that case being  $+270$  kOe. Presumably this orbital field arises from unpaired d-electrons at the Ir or Au sites in these alloys. Since these sites nominally have cubic symmetry, an orbital contribution is unexpected (it may arise through spin-orbit coupling in these heavy elements). Clearly hyperfine anomalies have yielded information in these cases that will be valuable in elucidating the origins of hyperfine fields.

## IX. ZERO-POINT SPIN DEVIATIONS

Spin-wave theories (55,56) of antiferromagnetism predict a deviation from perfect spin alignment, within each sublattice, in the completely ordered state. As  $T \rightarrow 0$  this effect should be manifest as a zero-point spin deviation  $\Delta_0$  given by

$$\bar{S}_z = S - \Delta_0 \quad ,$$

where  $S$  is the effective spin and  $S_z$  is the average  $z$  component at  $T = 0$ .

Anderson (55) gave the values  $\Delta_0 = 0.197$  for a two-dimensional (quadratic layer) lattice and  $\Delta_0 = 0.078$  for a cubic (NaCl type) lattice. Early attempts to observe  $\Delta_0$  in  $Mn^{2+}$  compounds met with difficulties because of hyperfine interactions from neighboring  $Mn^{2+}$  ions (57). In 1970, however, three groups reported the observation of  $\Delta_0$ .

Ôno, et al. (58) studied the hyperfine splitting of  $^{57}Fe$  in  $K_3Fe(CN)_6$ .

They cooled this salt as low as  $0.015^\circ K$  by adiabatic demagnetization (the Néel point is  $0.129^\circ K$ ). The effective spin of  $Fe^{3+}$  is  $1/2$  for this case, the crystal structure is monoclinic, and the spin structure is unknown. The hyperfine

structure tensor is anisotropic, and this introduces some uncertainty into the interpretation. However, Ono, et al. found a deviation in the hyperfine field of either  $(17.1 \pm 3)\%$  or  $(18.5 \pm 3)\%$ . This compares well with the value 15.6% given by Anderson's model for the cubic lattice with  $S = 1/2$ .

H. W. de Wijn, et al. (59) studied the temperature dependences of sublattice magnetization of the quadratic layer antiferromagnets  $K_2MnF_4$  and  $K_2NiF_4$  by following the temperature dependence of the NMR frequency of out-of-layer  $^{19}F$  nuclei. They made detailed analyses of these data and derived a value  $\Delta_0 = 0.20 \pm 0.03$  for the  $K_2NiF_4$  case ( $S = 1$  for  $Ni^{2+}$ ). This compares very well with the above spin-wave value of 0.197: these authors calculated a spin wave value of 0.18, which includes anisotropy effects.

Wagner et al. (60) studied the  $^{193}Ir$  Mössbauer resonance in  $(NH_4)_2IrCl_6$  down to  $0.04^\circ K$  in a dilution refrigerator ( $T_N = 2.16^\circ K$ ). This compound is cubic, and  $S = 1/2$  for  $Ir^{4+}$ . They found  $\Delta_0 = (18 \pm 1)\%$ , in good agreement with the result of Ono et al. (58) for  $K_3Fe(CN)_6$ .

These three investigations demonstrate the existence of zero-point spin deviation. They suggest that  $\Delta_0$  has the dependence on sublattice

dimensionality that is expected theoretically (i.e.  $\Delta_0 \sim 0.2$  for the two-dimensional case and  $\Delta_0 \sim 0.1$  for the three-dimensional sublattices). Actually  $\Delta_0$  is expected to be of order of magnitude  $1/2Z$ , where  $Z$  is the number of nearest neighbors (55).

## X. MOSSBAUER STUDIES OF HEAVY TRANSITION METAL COMPLEXES

Kaindl, et al. (61) summarized the systematic variations of isomer shifts with oxidation state in the 4d transition-series element Ru and the 5d elements Ir and Os. Resonances in  $^{99}\text{Ru}$ ,  $^{193}\text{Ir}$ , and  $^{189}\text{Os}$  were studied. Many of the shifts in  $^{99}\text{Ru}$  have been reported elsewhere (62-64), as were those in  $^{193}\text{Ir}$  (65,66). The isomer shifts for these three elements were discussed by Kaindl et al. (61) together with shifts in  $^{57}\text{Fe}$  compounds. They considered first the compounds in which the transition metal atom has "innocent" ligands such as halides,  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ , or  $\text{O}^{2-}$ . For these cases the shifts clustered together according to the oxidation state of the transition-metal atom. In all four elements the electron density at the nucleus increases monotonically with oxidation state, because of decreased shielding of the s electrons as d electrons are lost.

In complexes involving  $\text{CN}^-$  and  $\text{NO}^+$  ligands (e.g.  $\text{M}(\text{CN})_6^{n-}$ ), the transition element isomer shifts fell at positions corresponding to anomalously high electron densities. This effect was attributed to "back-bonding" of the  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  electron orbitals with empty  $\pi^*$  ligand orbitals. The d electron

population is decreased thereby, and the s electron density at the nucleus is enhanced by the decreased d shielding.

Until 1970 no systematic study of Au compounds by Mössbauer had been reported in detail. Three papers (67-69) on this topic appeared in 1970.

Neutral gold has a full d shell, but gold is usually regarded as a transition metal in its complexes. The Mössbauer spectroscopy of gold, however, is markedly different from that of the transition metals cited above. There are only two common oxidation states, Au(I) ( $5d^{10}$ ) and Au(III) ( $5d^8$ ). The isomer shift within each oxidation state varies over a wide range, with almost complete overlap between the Au(I) and Au(III) groups. The same is true of the quadrupole splitting. The isomer shifts and quadrupole splittings show a strong correlation within each oxidation state, as shown in Fig. 3. The isomer shift values fall in the order of the ligands in the spectrochemical series (67,68). In a semiquantitative way the isomer shifts and quadrupole splittings, and their correlations, can be understood on the basis of sp bonding in the linear Au(I) compounds and  $dsp^2$  bonding superimposed on a  $d^8(d_{x^2-y^2}^{-2})$  ionic core in the Au(III) compounds. Attempts to fit the results



quantitatively with atomic constants were not successful, however (69), and it seems clear that a more sophisticated theoretical treatment will be required.

## XI. IRON IN HEMOGLOBIN

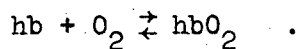
Lang et al. (70) succeeded in magnetically diluting a sample of hemin. They observed magnetic hyperfine structure, and found that hemin is magnetically similar to high-spin heme proteins.

Eicher and Trautwein (71) have studied the electronic structure of  $\text{Fe}^{2+}$  in hemoglobin. They analyzed their earlier quadrupole-splitting data (72) to calculate and predict the temperature-dependence of the magnetic susceptibility. Trautwein, Eicher, and Mayer (73) studied the spectrum of ferrous ion in anhydrohemoglobin. They interpreted the spectrum as arising from two superimposed quadrupole-split spectra, corresponding to a high-spin ( $S = 2$ )  $\text{Fe}^{2+}$  and a low spin ( $S = 0$ )  $\text{Fe}^{2+}$ . Comparison with the spectra of  $^{57}\text{Fe}^{2+}$  in hemoglobin and myoglobin led them to conclude that when hemoglobin loses water to form anhydrohemoglobin the high-spin  $\text{Fe}^{2+}$  in the  $\alpha$  chain is unaffected, but that the  $\beta$ -chain  $\text{Fe}^{2+}$  goes to the low-spin state. They suggested that this change accompanies the coordination of a sixth nitrogen atom, belonging to the distal histidine, to  $\text{Fe}^{2+}$ . Trautwein, et al. (74) took Mössbauer spectra of rat hemoglobin enriched in vivo in  $^{57}\text{Fe}$ . They inferred the low-energy term schemes of

$\text{Fe}^{2+}$  in deoxyhemoglobin(hb), oxyhemoglobin( $\text{hbO}_2$ ), and carbonylhemoglobin( $\text{hbCO}$ ).

They concluded that the  $^1\text{A}_1$  ground state of  $\text{hbCO}$  lies lower in energy than either the  $\Gamma$  ground state of  $\text{hbO}_2$  or the  $^5\text{B}_2$  ground state of hb, in agreement with the known equilibrium behavior of hb with CO and  $\text{O}_2$ .

Trautwein and Schretzmann (75) postulated, on the basis of Mössbauer spectra of iron in hb and  $\text{hbO}_2$ , a double bond between the heme iron and  $\text{O}_2$  in  $\text{hbO}_2$ . They suggested that the electronic excitation is restricted to the oxygen. In the Griffith orientation of  $\text{O}_2$  they postulate a  $\pi-\pi^*$  transition and in the Pauling orientation an  $n-\pi^*$  transition. In either case the remaining filled  $\pi$  or n orbital can combine with the singly populated Fe ( $d_{z^2}$ ) orbital in a  $\sigma$  bond, and a  $\pi$  bond is formed between the singly occupied  $d_{yz}$  or  $d_{xz}$  orbital and the singly populated  $\pi^*$  orbital of  $\text{O}_2$ . The formation of a double bond is facilitated by a  $^3\text{E}$  intermediate ( $S = 1$ ) spin state of  $\text{Fe}^{2+}$ . Trautwein and Schretzmann suggested that this may be the key to the reversibility of the reaction



## XIII. OTHER TOPICS

Many very good papers in Mössbauer spectroscopy appeared in 1970. A small fraction of these were discussed above in connection with topics that the reviewer felt were of general interest. A few others are mentioned briefly below.

The effects of particle size on Mössbauer spectra have been studied in several ways. Among these, Fabritchnyi et al. (76) reported surface effects associated with thermal annealing of  $\alpha$ - and  $\beta$ -stannic acid. Large changes in  $\langle x^2 \rangle$  were observed, especially for the  $\alpha$  form, when the particle diameter was less than 25 Å. For particles of larger diameters,  $\langle x^2 \rangle$  did not increase further with crystal size. Afanas'ev et al. (77) studied superparamagnetism in ferromagnetic particles of FeNi alloys (37% Ni) through their  $^{57}\text{Fe}$  absorption spectra. They related the fluctuation time  $\tau$  of an entire particle to the magnetic anisotropy energy per unit volume,  $K$ , by  $\tau = \tau_0 \exp(KV/T)$ . As the particle size was increased from  $d = 120$  Å,  $KV$  appeared to increase, decrease, and increase again. Afanes'ev et al. explained this behavior in terms of the transition from homogeneous magnetization in small particles to domain structure

in larger particles. Ruppin (78) has made a theoretical study of the recoilless fraction  $f$  in microcrystals, using a lattice-dynamical model. He found that  $f$  increases with increasing stiffness of binding to the surrounding medium. He also discussed the failure of the Debye approximation to predict  $f$  for microcrystals. Schroerer, et al. (79) studied the isomer shift in gold microcrystals and showed that it is correlated with the lattice contractions in these microcrystals.

A large number of metals and alloy systems have been studied. Dunlap et al. (80) found two quadrupole spectra, which they attributed to inequivalent sites, in  $\alpha$ -Np. Hirst and Seidel (81) studied local moments of Er in Zr, and found that the hyperfine constant  $A$  of Er is 15% larger than that of  $\text{Er}^{3+}$  in insulators. This important result, which they attributed to conduction electron polarization at the impurity, awaits quantitative explanation. Hirst (82) gave a very good concise discussion of relaxation theories in a paper on the ErZr system.

Small variations of isomer shifts with composition were observed in SnSb solid solutions by Ruby et al. (83) and in MnSn alloys with the  $\beta$ -Mn

structure by Kimball and Sill (84). There are now many examples of such an insensitivity of isomer shift to composition in alloy systems. They suggest an "electroneutrality" principle which has yet to be quantitatively formulated in terms of shielding concepts. Patterson et al. (85) made a study of several Au-Mn intermetallic compounds. Among their many results was the observation of a 7% increase in the hyperfine field at Au in  $\text{Au}_2\text{Mn}$  as the pressure was raised to 46 kbars. They suggested that this may arise from uncoiling of the Mn spin helix. Trumpy et al. (86) studied compounds and solid solutions of Fe and Sn by Mössbauer spectroscopy on both  $^{57}\text{Fe}$  and  $^{119}\text{Sn}$ . They were able to relate hyperfine fields to coordination number and isomer shifts to bond number, but found  $H_{\text{hf}}(\text{Fe})$  rather insensitive to the degree of conduction-electron polarization. Neither  $H_{\text{hf}}(\text{Fe})$  nor  $H_{\text{hf}}(\text{Sn})$  was generally proportional to the magnetic moment.

Wertheim et al. (87) studied an anomaly in the centroid shift of the  $^{57}\text{Fe}$  resonance in Fe-doped  $\text{V}_2\text{O}_3$  near the high-temperature (575°K) metal-insulator transition. Comparison of these results with those for iron in Cr-doped  $\text{V}_2\text{O}_3$  led them to infer that the anomaly represented a gradual return from the metallic

to the insulating state. Khimich, et al. (88) found very complicated  $^{57}\text{Fe}$  spectra in hexagonal ferrites of the M structure. They interpreted these spectra in terms of four distinct sublattices in  $\text{BaFe}_{12}^{\text{O}}_{19}$  and  $\text{SrCo}_{0.42}\text{Ti}_{0.42}\text{Fe}_{11.16}^{\text{O}}_{19}$ . Lagunov, et al. (89) studied quadrupole broadening of the  $^{57}\text{Fe}$  line in Cu, using a  $^{57}\text{CoCu}$  source, as a function of the temperature of tempering after deformation. The line width showed a maximum near  $150^\circ\text{C}$ . Presumably the  $^{57}\text{Co}$  atoms go to defects, but above  $150^\circ\text{C}$  tempering is effective in removing defects.

De Barros, et al. (90) studied the spectrum of  $^{57}\text{Co}$  in diamond. The source was prepared by ion implantation. Two equal-intensity peaks were found, showing that Co atoms go into interstitial positions. The effect was small, as expected, although diamond has a very high Debye temperature. Begum (91) searched for isotope effects in iron. He compared the temperature shifts of  $^{57}\text{Fe}$  in a  $^{54}\text{Fe}$  lattice with that of  $^{57}\text{Fe}$  in a  $^{56}\text{Fe}$  lattice, finding

$$(\Delta E_{54} - \Delta E_{56})_{77^\circ\text{K}} - (\Delta E_{54} - \Delta E_{56})_{290^\circ\text{K}} = (0.9 \pm 0.6) \times 10^{-15} \text{E}_\gamma$$

If one naively considers only the Debye temperature of the host, an effect of  $4.2 \times 10^{-15} \text{E}_\gamma$  would be expected. However, the correct effective Debye temperature

is given by

$$\theta_{\text{eff}} = \theta_{\text{host}} \left( \frac{M_{\text{host}}}{M_{\text{impurity}}} \right)^{1/2},$$

and no net effect should be observed. Isaak and Longworth (92) searched for variations in the  $^{57}\text{Fe}$  hyperfine fields in host lattices of  $^{54}\text{Fe}$ ,  $^{56}\text{Fe}$ , and  $^{57}\text{Fe}$ . The fields were all found to be the same to within 3 parts in  $10^4$ .



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TABLE 1. Mössbauer-Photoeffect Interferences. Summary of Results

Nucleus	$E_\gamma$ , keV	Multipolarity	$2\xi_{(expt)}$	$2\xi_{(theo)}$	Ref
$^{153}\text{Eu}$	97.4	E1	0.022(5) <sup>a</sup>	0.029	10
$^{155}\text{Gd}$	86.5	E1	0.05(1)	0.035	10
	105.3	E1	0.035(10)	0.026	10
$^{161}\text{Dy}$	25.6	E1	0.07(1)	0.067 <sup>b</sup>	10
	25.6	E1	0.078(11)	0.077 <sup>b</sup>	9
	25.6	E1 <sup>c</sup>	0.102(15)	0.108	9
	74.5	E1	0.06(1)	0.05	10
$^{181}\text{Ta}$	6.25	E1	0.30(1)	0.31	8
$^{119}\text{Sn}$	23.8	M1			12

<sup>a</sup>Errors in last place given parenthetically.

<sup>b</sup>Two different estimates. See Refs. (9) and (10).

<sup>c</sup>Conversion electrons observed.

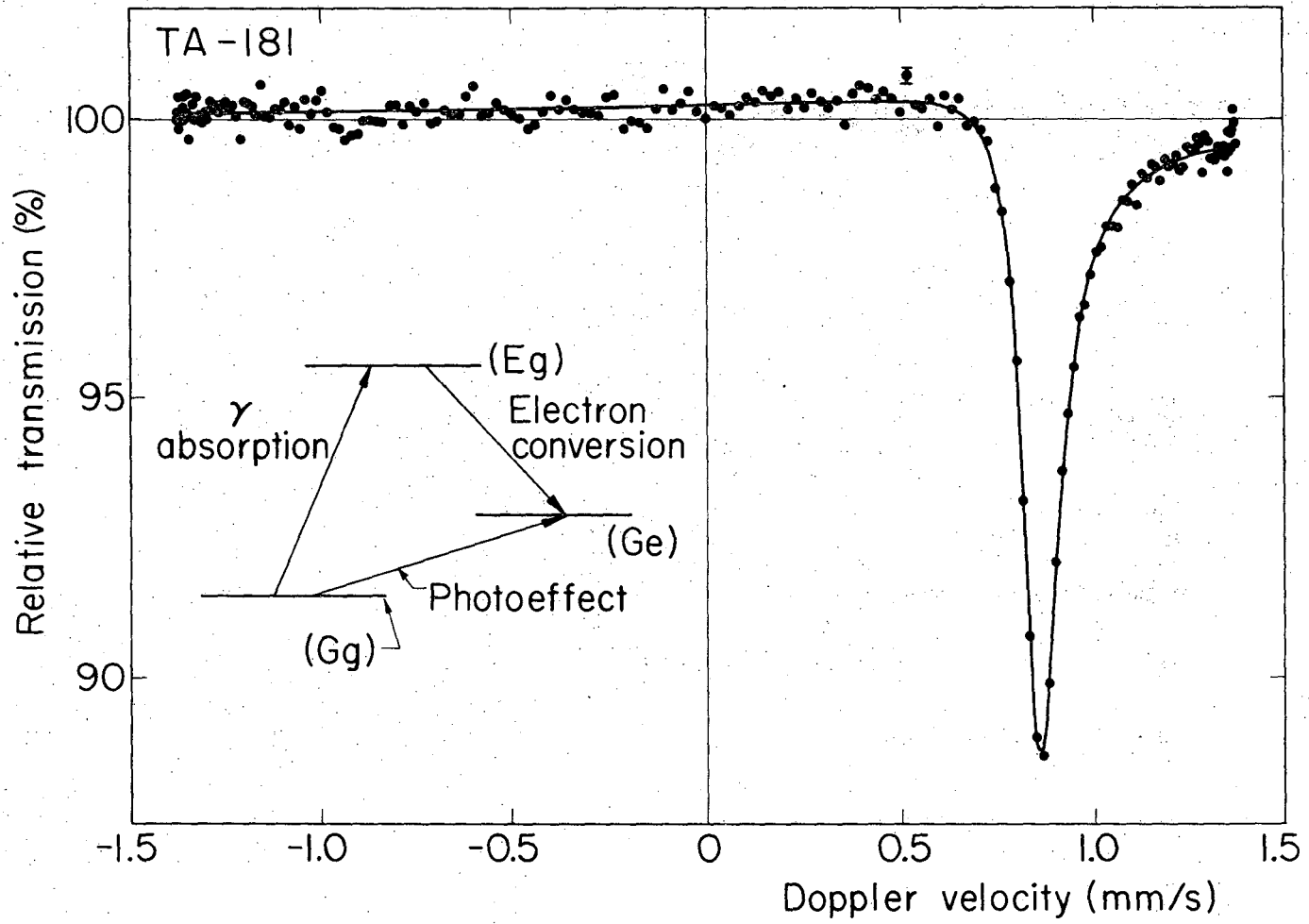
## FIGURE CAPTIONS

Fig. 1. Resonant absorption-photoeffect interference in  $^{181}\text{Ta}$ , using a W metal source and a Ta metal absorber. The theoretical curve was fitted to the data, giving  $2\xi = 0.31 \pm 0.01$  (G. Kaindl and D. Salomon, private communication). The level scheme on the left illustrates the two interfering processes that form the state (Ge) with the nucleus in the ground state G and the electron configuration in an excited hole state e.

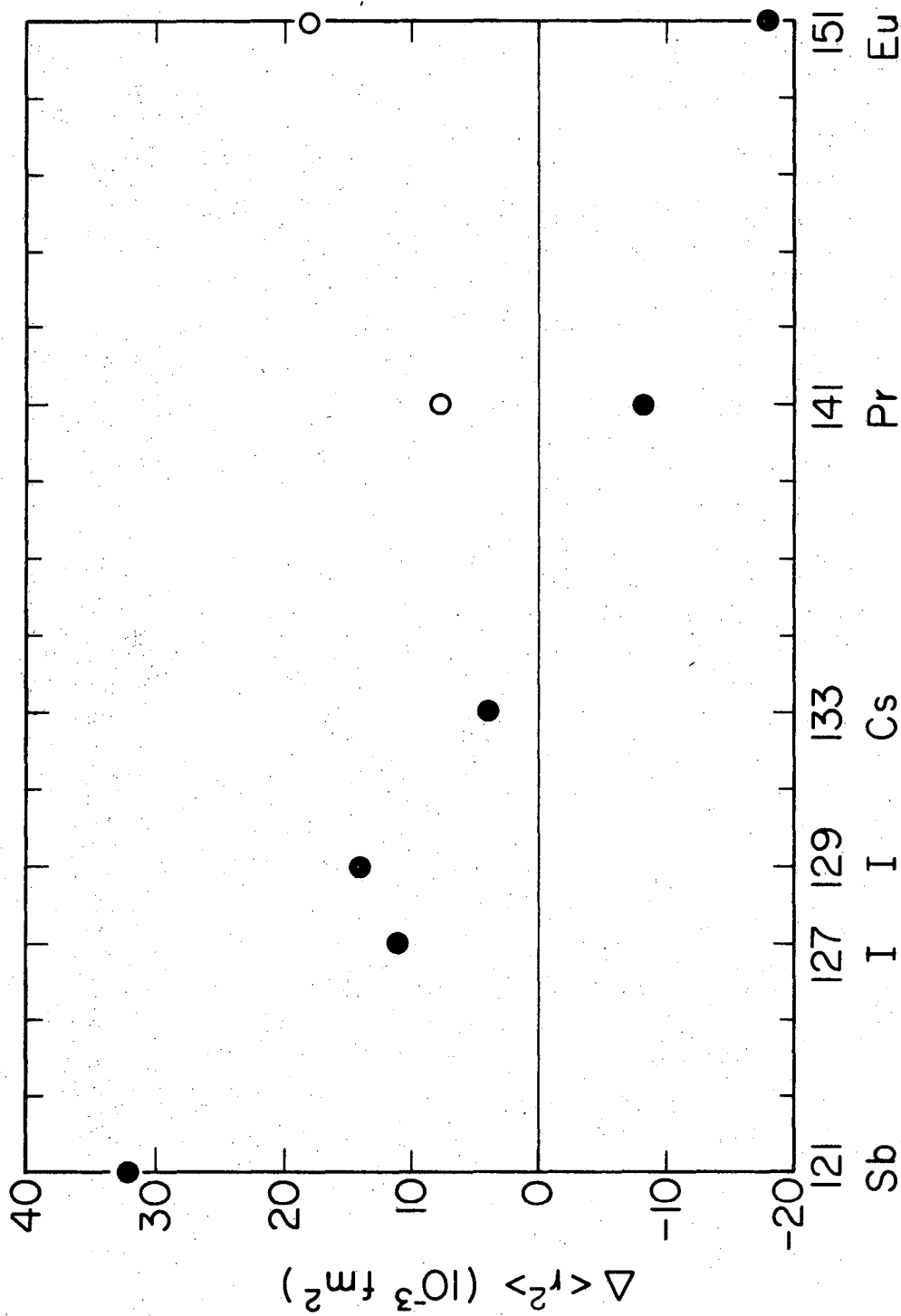
Fig. 2. Variation of  $\Delta \langle r^2 \rangle = \langle r^2(d_{5/2}) \rangle - \langle r^2(g_{7/2}) \rangle$  for Mössbauer nuclei in the  $2d_{5/2} - 1g_{7/2}$  proton subshell. Kalvius has pointed out the symmetry in  $\Delta \langle r^2 \rangle$  for particle states in nuclei of atomic number Z and hole states in nuclei of atomic number  $64-Z$  (open circles).

Fig. 3. Quadrupole splitting-isomer shift correlation plot for gold compounds, from data in Refs. (67-69) ( $\bullet$  = auric compounds,  $\circ$  = aurous compounds). Only the magnitude of the quadrupole splittings were measured. In plotting the data, we have assigned signs to the quadrupole splittings in several auric compounds. In fact the aurous compounds are believed to have  $e^2qQ < 0$ , while most of the auric compounds should have  $e^2qQ > 0$ , on the basis of sp and  $dsp^2$  bonding, respectively.

Fig. 1



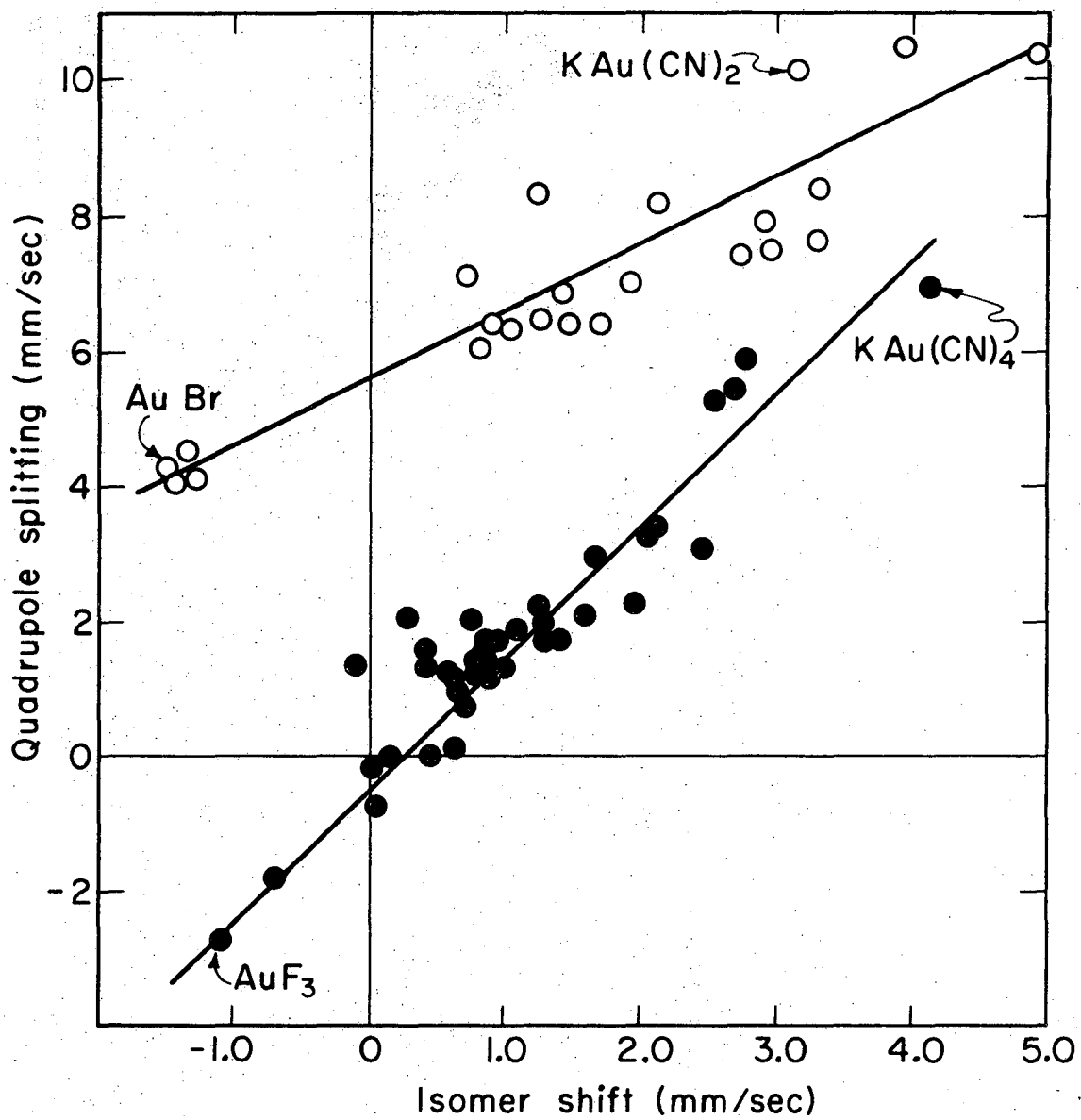
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A →

Fig. 2



XBL712-2830

Fig. 3

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