tion. As noted above, in the limit of high-barrier height, the tunneling splitting equals -2α. If, instead of a spherical potential, an ellipsoidal potential is utilized, we find that α is again given by Eq. (17). Correction terms to this expression do not become important until the ratio of semimajor axis to semiminor axis exceeds 4.5:1. The values of the displacement χ^0 and the tunneling splitting δ calculated on the basis of a spherical potential should accordingly be a very good approximation even to rather nonspherical potentials.

V. CONCLUSION

The paraelectric-resonance results are interpretable in a consistent way through a model in which the OH^- ion moves in a 3-dimensional set of harmonic potentials. The zero-field-energy splitting and the dipole moment, calculated from this model, agree with the values obtained in a number of other experiments. The results further support the concept that the c.m. of the OH^- is displaced from the alkali-halide lattice site.

ACKNOWLEDGMENTS

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Mössbauer Effect in Ir^{193} in Intermetallic Compounds and Salts of Iridium* †

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Recoilless-absorption measurements of the 73-keV γ rays of Ir^{193} have been carried out using an Os^{193} source in metallic form and absorbers of Ir metal, $Fe_{0.99}Ir_{0.01}$, various rare-earth–iridium (RIr_2) intermetallic compounds, and a few trivalent and tetravalent Ir salts. From the measurements, the assignment of spin $\frac{1}{2}$ to the 73-keV level was confirmed, and the ratio of the magnetic moment of this level to the magnetic moment of the ground level was found to be 3.0 ± 0.1. The small value obtained for the magnetic moment of the first excited state can be explained by the core-excitation model of de Shalit. The results yielded a value of $\delta^2=0.37\pm0.06$ for the $E2/M1$ mixing ratio of the 73-keV transition. The absolute values of the internal magnetic fields acting on the Ir nuclei in iron and in the RIr_2 compounds were deduced. The dependence of these fields on the rare-earth element was found to follow approximately the predictions of the Kasuya-Yosida theory on conduction-electron polarization, though an exact fit between this theory and experiment was not obtained. The electric field gradients acting on the Ir nuclei in the hexagonal Os metal lattice, in some Ir salts, and in the various RIr_2 compounds were deduced. Isomer-shift measurements indicate that the sign of $\Delta\langle r^2\rangle$, the difference in the mean-square charge radii between the first excited state and ground state of Ir^{193}, is positive.

INTRODUCTION

It is generally believed that the ferromagnetic interactions in the pure rare-earth metals and in intermetallic compounds containing a rare-earth metal and a diamagnetic metal are essentially indirect interactions between the localized $4f$ electrons of the rare-earth ions via the conduction electrons. According to this model, the effective magnetic field acting on the nucleus of a diamagnetic ion, which is either an impurity in a rare-earth metal or forms with it an intermetallic compound, is produced by the conduction electrons, which are polarized by their interaction with the $4f$ electrons of the rare-earth ions. The main object of the present measurements was to investigate the dependence of the effective magnetic field acting on the nucleus of the nonmagnetic ion on the properties of the rare-earth ion with which it forms an intermetallic compound. In order to achieve this, measurements of the effective field acting on Ir nuclei in various rare-earth intermetallic RIr_2 compounds were carried out.

The investigated RIr_2 compounds belong to the family of the Laves phase compounds of the RM_2 type, where R is a lanthanide ion and M can be one of several possible other ions. These compounds have a cubic unit cell and the point symmetry of the rare-earth sites in them is also cubic. Bozorth *et al.* have carried out magnetiza-

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tion measurements on the RIr_2 compounds.[1] They found that most of them become ferromagnetic at low temperatures, and that the Curie temperatures appear to be correlated with the $J(J+1)(g_J-1)^2$ values of the rare-earth ions.

Some measurements of the internal fields acting on the nuclei of diamagnetic ions dissolved as impurities in the rare-earth metals have previously been published.[2,3] These measurements were carried out for the heavy rare-earth metals (Gd and above), all of which have the same hexagonal close-packed structure. Some of the heavy rare-earth metals are not ferromagnetic at low temperatures but have a variety of complicated magnetic structures, which makes the comparison of fields acting on the nuclei of diamagnetic impurities in them somewhat ambiguous.

The internal fields acting on the nuclei of diamagnetic ions in ferromagnetic rare-earth intermetallic compounds have so far been investigated only for two systems of compounds: Bosch *et al.*[3] measured the internal fields at the Sn nuclei in the R_2Sn compounds. These measurements were carried out for the heavy rare-earth ions. The results were quite similar to those obtained in the present work for the same heavy rare-earth ions. Borsa *et al.*[4] have carried out some Mössbauer-effect measurements on the RSn_3 system. Only compounds with the light rare-earth metals were investigated and no magnetic splittings were observed. All the RIr_2 compounds investigated in the present work have the same crystal structure and are ferromagnetic at 4.2°K. Internal magnetic fields acting on Ir nuclei could be measured in compounds with many of the light and the heavy rare earths.

The internal magnetic fields acting on the Ir nuclei in these compounds are expected to be proportional to the conduction-electron polarizations. A quantitative theory dealing with conduction-electron polarization was given by Kasuya and Yosida.[5,6] We compare some of our experimental results to the predictions of this theory although we are aware of the fact that the calculations in this theory have been done in terms of free-electron conduction bands and the resulting oscillating spin densities must be viewed with caution, particularly in discussions of the region around a nucleus.

The measurements in the present work were carried out utilizing the Mössbauer effect in the 73-keV transition of Ir^{193}. Some results of recoilless absorption measurements on the 73-keV γ rays of Ir^{193} were previously reported by Bussiere de Nercy *et al.*,[7,8] by Thomson *et al.*,[9] and by Huntzicker *et al.*[10]

The spin of the ground level of Ir^{193} is $\frac{3}{2}+$.[11] From the analysis of hyperfine splittings in atomic spectra, the following values were found for the magnetic and quadrupole moments of the ground level: $\mu_1=0.17\pm0.03$ nm and $Q_1=1.0\pm0.5$ b.[11] Very recently, NMR measurements on Ir^{193} in Ir metal were reported, giving a value of 0.15887 ± 0.00009 nm for the effective magnetic moment of the ground state, uncorrected for Knight shifts and diamagnetic shifts.[12] The half-life of the 73-keV level is known to be $T_{1/2}=6.2\pm0.3\times10^{-9}$ sec.[13] The most probable spin assignment to the 73-keV level is $\frac{1}{2}+$. In order to confirm this assignment and to measure the magnetic moment of this level, and the $E2/M1$ mixing ratio δ^2 of the 73-keV transition, a Mössbauer measurement was carried out with an $Ir_{0.01}Fe_{0.99}$ absorber. This absorber was chosen as it is known to have cubic symmetry and a high internal magnetic field ($\sim1.3\times10^6$ Oe) acting on the Ir nuclei.[14] The value found for the magnetic moment of the 73-keV level is much smaller than the value predicted by the shell model, and can be explained by the core-excitation model of de-Shalit.[15,16]

Isomer shifts between various Ir compounds were also measured. These measurements show that the sign of $\Delta\langle r^2\rangle$, the difference in the mean-square radius of the charge distribution between the 73-keV level and the ground level of Ir^{193}, is positive. Only a very crude value for $\Delta\langle r^2\rangle$ was deduced, as it is very difficult to estimate accurately the differences between the electron densities at the Ir nuclei in the various compounds.

EXPERIMENTAL DETAILS

The source used in all the measurements was Os^{193} in metallic form. It was produced by neutron irradiation of Os metal enriched to 99% in Os^{192}. The 73-keV γ rays of Ir^{193} were detected by a Ge(Li) detector in order to resolve them from the Ir Kα x rays. The γ spectrum is shown in Fig. 1.

The absorbers used were $Ir_{0.01}Fe_{0.99}$, $NdIr_2$, $PrIr_2$,

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[1] R. M. Bozorth, B. T. Matthias, H. Suhl, E. Cornzwit, and D. D. Davis, Phys. Rev. **115**, 1595 (1959).

[2] S. G. Cohen, N. Kaplan, and S. Ofer, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1965), p. 233.

[3] D. Bosch, F. Pobell, and P. Kienle, Phys. Letters **22**, 262 (1966).

[4] F. Borsa, R. G. Barnes, and R. A. Reese, Phys. Status Solidi **19**, 359 (1967).

[5] T. Kasuya, Progr. Theoret Phys. (Kyoto) **16**, 45 (1956).

[6] K. Yosida, Phys. Rev. **106**, 893 (1957).

[7] A. Bussiere de Nercy, M. Langevin, and M. Spighel, J. Phys. Radium **21**, 288 (1960).

[8] A. Bussiere de Nercy, M. Langevin, and M. Spighel, Compt. Rend. **250**, 1031 (1960).

[9] J. O. Thomson, A. H. Werkheiser, and M. W. Lindauer, Rev. Mod. Phys. **36**, 357 (1964).

[10] J. J. Huntzicker, E. Matthias, S. S. Rosenblum, and D. A. Shirley, University of California Radiation Laboratory Report No. UCRL-11828, 1964, pp. 57–8 (unpublished).

[11] K. Murakawa and S. Suwa, Phys. Rev. **87**, 1048 (1952).

[12] A. Narath and D. C. Barham, Bull. Am. Phys. Soc. **12**, 314 (1967).

[13] H. de Waard, Physica **20**, 41 (1954).

[14] A. V. Kogan, Y. O. Kul'kov, L. P. Nikitin, N. M. Reĭnov, and M. F. Stel'makh, Zh. Eksperim. i Teor. Fiz. **45**, 1 (1963) [English transl.: Soviet Phys.—JETP **18**, 1 (1964)].

[15] A. Braunstein and A. de Shalit, Phys. Letters **1**, 264 (1962).

[16] A. de Shalit, Phys. Letters **15**, 170 (1965).

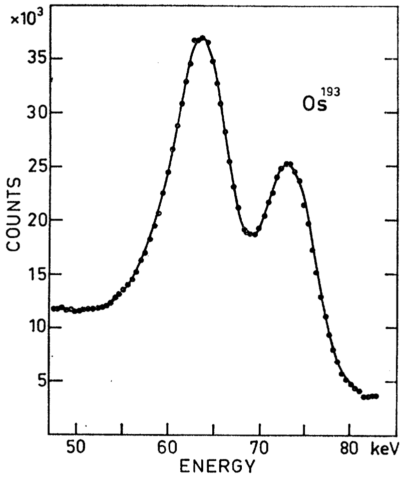

FIG. 1. γ-ray spectrum of an Os^{193} source taken with a Ge(Li) detector.

$SmIr_2$, $GdIr_2$, $TbIr_2$, $DyIr_2$, $HoIr_2$, K_3IrCl_6, IrI_3, IrO_2, $(NH_4)_2IrCl_6$, and K_2IrCl_6. The intermetallic compounds were prepared by melting stoicheiometric amounts of Ir and rare-earth metals. This was done in an induction furnace using a quartz crucible and an argon atmosphere. The linear velocity drive was similar to the one described by Cohen *et al.*[17] and the recoilless absorption spectra was recorded automatically on a multichannel pulse-height analyzer working in the multi-scaler mode. Most of the measurements were carried out with both source and absorber at the same temperature using the cryostat, described in Ref. 18, filled with liquid helium, hydrogen, or nitrogen. For measurements where the temperature of the absorber was different from that of the source, two separate cryostats were used, one for the source and one for the absorber.

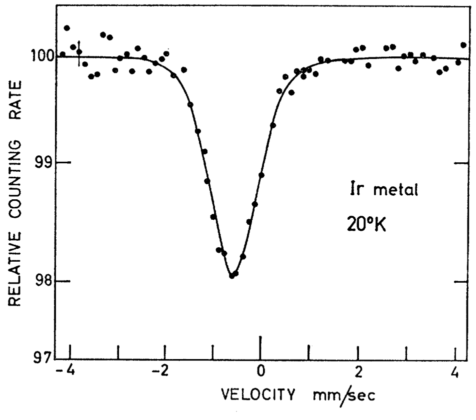

FIG. 2. Recoilless absorption by Ir metal at 20°K of the 73-keV γ rays of Ir^{193} as a function of relative velocity between source and absorber.

EXPERIMENTAL RESULTS

A. Ir Metal Absorber

The recoilless-absorption measurements in Ir metal were carried out with a 19-mg/cm^2 absorber at 20 and 90°K and with a 140-mg/cm^2 absorber at 90°K. The absorption spectrum obtained at 20°K is shown in Fig. 2. The width at half-height of the three experimental spectra was 1.10 ± 0.05 mm/sec. The width expected (from the lifetime of the 73-keV level) for emission and absorption lines with natural widths is 0.6 mm/sec. As the width is the same for the three absorbers and as the Ir metal absorber has cubic symmetry, the broadening very probably results mainly from the internal interactions in the Ir^{193} source in the hexagonal Os lattice. The absorption line observed is therefore essentially a superposition of two lines of natural linewidth, resulting from the quadrupole interaction of the Ir^{193} ground state in the hexagonal Os lattice. From the width of the absorption lines a value of 13 ± 2 Mc/sec is derived for the quadrupole interaction parameter ($eq_{\mathrm{eff}}Q/4$) of the ground level of Ir^{193} in Os metal (q_{eff} contains shielding factors). Taking into account the value of 1.0 ± 0.5 b for Q_1,[11] we find that the electric field gradient at the Ir nuclei in Os metal is 13_{-5}^{+13} Mc/sec per barn. This value is in good agreement with the value derived by Grodzins *et al.*,[19] from angular-correlation measurements, for $eq_{\mathrm{eff}}/4$ acting on Os nuclei in Os metal [$22\pm$ 4 Mc/sec per b].

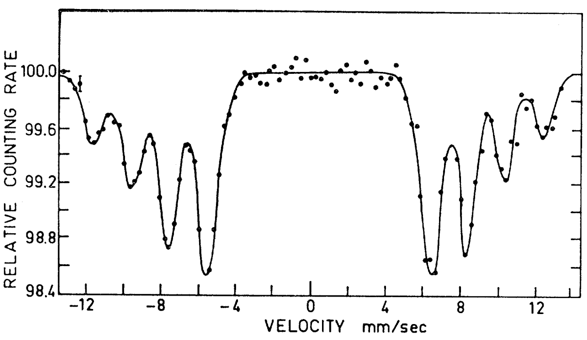

FIG. 3. Recoilless absorption by $Fe_{0.99}Ir_{0.01}$ at 4.2°K of the 73-keV γ rays of Ir^{193} as a function of relative velocity between source and absorber.

The isomer shift between the Ir in Os metal source and the Ir metal absorber was found to be $0.55\pm$ 0.05 mm/sec.

B. $Ir_{0.01}Fe_{0.99}$ Absorber

The recoilless-absorption spectrum in a 1-gm/cm^2 $Ir_{0.01}Fe_{0.99}$ absorber at 4.2°K is shown in Fig. 3. Eight

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[17] R. L. Cohen, P. G. McMullin, and G. K. Wertheim, Rev. Sci. Instr. **34**, 671 (1963).

[18] U. Atzmony, A. Mualem, and S. Ofer, Phys. Rev. **136**, B1237 (1964).

[19] L. Grodzins and Y. W. Chow, Phys. Rev. **142**, 86 (1966).

well-resolved lines were obtained. The width of each individual line is 1.1±0.1 mm/sec, which is the same as the linewidth obtained with an Ir metal absorber. In a previous measurement,[10] in which the source was Os^{193} in Fe and the absorber was Ir metal, the lines were hardly resolved.

The analysis of the recoilless-absorption spectrum confirms unambiguously the assignment of spin $\frac{1}{2}$ to the 73-keV level and yields the following results for the hyperfine splitting parameters:

$$|G_1| = |g_1\mu_n H_{\text{eff}}| = 1.98 \pm 0.04 \text{ mm/sec}$$

$$= (4.82 \pm 0.10) \times 10^{-7} \text{ eV},$$

$$|G_2| = |g_2\mu_n H_{\text{eff}}| = 17.96 \pm 0.09 \text{ mm/sec}$$

$$= (43.7 \pm 0.2) \times 10^{-7} \text{ eV},$$

and

$$g_2/g_1 = 9.1 \pm 0.3,$$

$$eqQ_1/4 \leq 0.08 \text{ mm/sec} = 1.9 \times 10^{-8} \text{ eV},$$

where g_1 and g_2 are the gyromagnetic ratios of the ground level and the 73-keV level, respectively, and Q_1 is the quadrupole moment of the ground level.

From the observed line intensities and the theoretical Clebsch-Gordan coefficients for $M1$ and $E2$ transitions between states with spins $\frac{3}{2}$ and $\frac{1}{2}$, a value of 0.37±0.06 was deduced for the mixing ratio δ^2. The values found for g_2/g_1 and δ^2 are in agreement with those estimated by Huntzicker *et al.*[10] ($g_2/g_1 \sim 10$ and $\delta^2 \sim 0.4$).

Taking into account the recently measured effective magnetic moment of the ground level of Ir^{193} (0.15887± 0.00009 nm),[12] a value of 0.48 nm is found for the magnetic moment of the 73-keV level. The value given for the magnetic moment of the ground level[12] is uncorrected for possible Knight and diamagnetic shifts; we estimate (from Knight-shift measurements on Pt metal[20]) the possible error on the magnetic moment of the 73-keV level to be less than 5%.

TABLE I. Curie temperatures, lattice constants, quadrupole and magnetic interaction constants, and effective magnetic fields at the Ir nuclei in RIr$_2$ compounds.

Compound	Curie temperature (°K)	Lattice constant a (Å)	$\epsilon_1 = eqQ_1/4$ (Mc/sec)	$\lvert G_2 \rvert$ (Mc/sec)	$\lvert H_{\text{eff}} \rvert$ (kOe)
$PrIr_2$	16	7.621	109±4	34	46±9
$NdIr_2$	11.8	7.605	106±6	35	48±9
$SmIr_2$	37		106±4	65	89±13
$GdIr_2$	88	7.550	103±4	141	192±14
$TbIr_2$	45		106±4	122	167±10
$DyIr_2$	23		103±4	68	93±10
$HoIr_2$	12		100±4	29	40±8

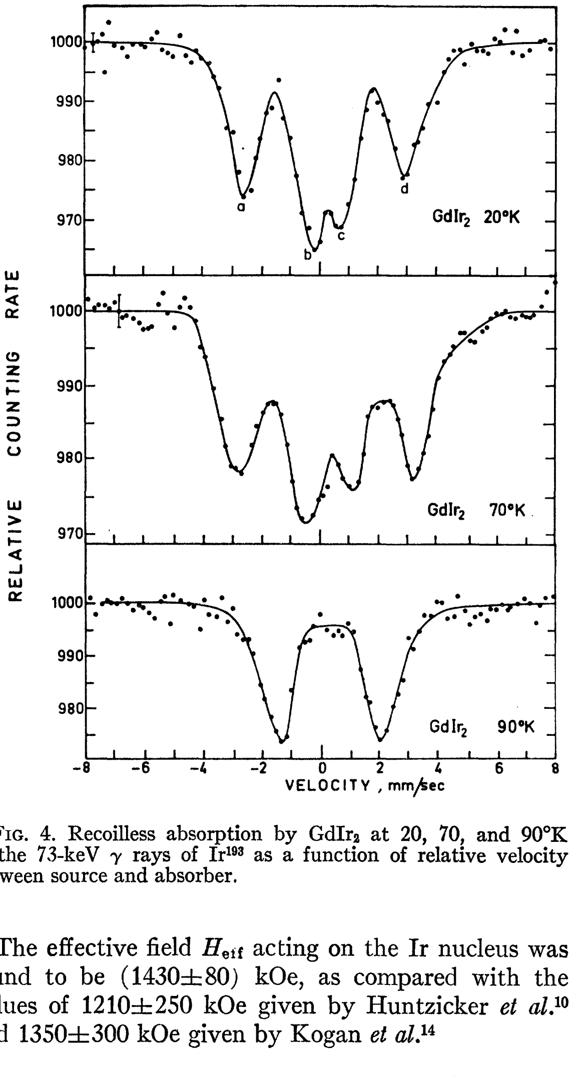

FIG. 4. Recoilless absorption by $GdIr_2$ at 20, 70, and 90°K of the 73-keV γ rays of Ir^{193} as a function of relative velocity between source and absorber.

The effective field H_{eff} acting on the Ir nucleus was found to be (1430±80) kOe, as compared with the values of 1210±250 kOe given by Huntzicker *et al.*[10] and 1350±300 kOe given by Kogan *et al.*[14]

C. RIr$_2$ Absorbers

Mössbauer experiments were carried out using intermetallic compounds of Ir with the following rare-earth metals: Pr, Nd, Sm, Gd, Tb, Dy, and Ho. All the measurements, except those with $GdIr_2$ were carried out with both source and absorber at the same temperature, once in liquid nitrogen and once in liquid helium. All these compounds are ferromagnetic at 4.2°K and their Curie temperatures are below 90°K.[1] (The Curie temperatures are given in Table I.) Above the Curie temperatures, all the spectra consist of two absorption lines. The widths at half-height of each line is equal to 1.1±0.1 mm/sec. The absorption spectrum obtained with $GdIr_2$ at 90°K is shown in Fig. 4 and is typical for the absorption spectra obtained above the Curie temperatures for the various compounds. The two lines arise from the quadrupole splitting of the $\frac{3}{2}+$ ground state. In Table I, the quadrupole splitting parameters derived for the various RIr$_2$ compounds are sum-

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[20] A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. 134, A650 (1964).

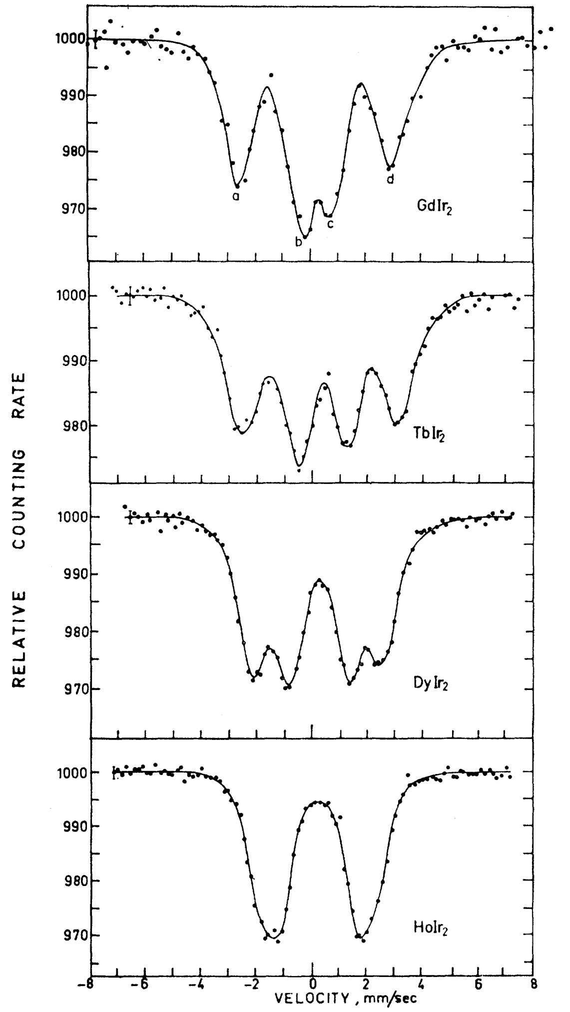

FIG. 5. Recoilless absorption at 4.2°K by $GdIr_2$, $TbIr_2$, $DyIr_2$, and $HoIr_2$ of the 73-keV γ rays of Ir^{193} as a function of relative velocity between source and absorber.

marized. These parameters are almost equal for all the compounds, but they show small systematic variations, which can be attributed to the change in the interatomic distances. The gradients produced by external electron charges are expected to be inversely proportional to the volumes of the unit cells. As seen from Table I, the trend of the variations of the quadrupole splitting parameters seems to be consistent with such a relation between q_{eff} and a^3.

With the $GdIr_2$ absorber, measurements were carried out for absorber temperatures ranging from 20 to 90°K, while the source was kept at 90°K. Some of these spectra are shown in Fig. 4. Below the Curie temperature, the spectra are split into four lines. The separations between the first and second lines and between the third and fourth lines increase with decreasing temperature, but the positions of the centroids of each of these couples remain unchanged. The separations between the centroids are equal to the quadrupole splittings above the Curie temperature.

Figures 5 and 6 show the absorption spectra obtained for various intermetallic absorbers with both source and absorber at 4.2°K. Some of them consist of four well-resolved absorption lines. As with the $GdIr_2$ absorber, the separations between the centroids of the first and second and between the third and fourth lines are equal to the respective quadrupole splittings. The other spectra consist of two lines which are broadened compared to the absorption lines obtained with the same absorbers above their respective Curie temperatures.

The Ir ions in these cubic Laves phase compounds occupy the four corners of a tetrahedron. This may give rise to magnetically unequal sites of the Ir ions, according to the angle θ, between the axis of easy magnetization and the axis of the axially symmetric field gradients. If the axis of easy magnetization is in the (1, 1, 1) direction as in $ZrFe_2$,[21] two unequal sites exist with relative populations of 1:3. For the first site $\theta=0°$ and

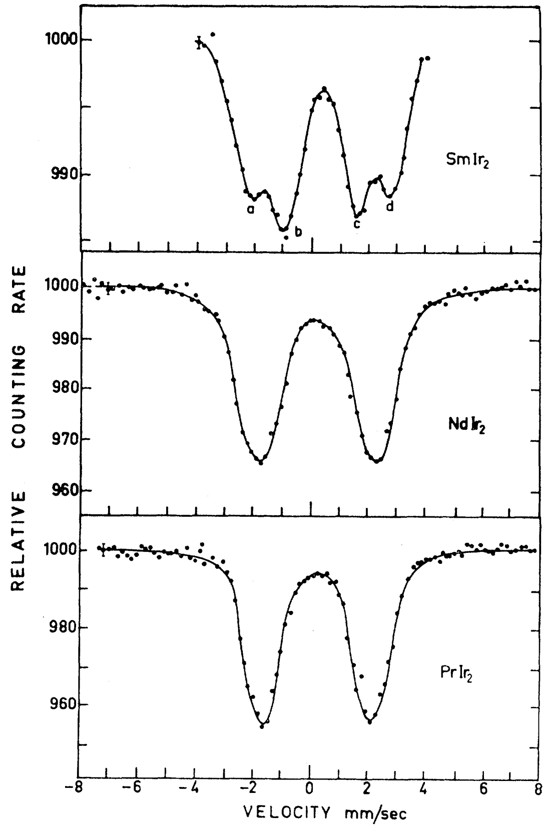

FIG. 6. Recoilless absorption at 4.2°K by $SmIr_2$, $NdIr_2$, and $PrIr_2$ of the 73-keV γ rays of Ir^{193} as a function of relative velocity between source and absorber.

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[21] G. K. Wertheim, V. Jaccarino, and J. H. Wernick, Phys. Rev. 135, A151 (1964).

for the second $\theta = 70°\ 32'$. The effective magnetic fields may be different in the two sites. (In $ZrFe_2$, Wertheim *et al.* found a difference of 7.6% between the values of H_{eff} at the Fe nuclei in the two sites.[21])

We do not know the direction of easy magnetization in the RIr_2 compounds, but a simple analysis shows that the four lines obtained in the resolved spectra are mainly produced by the magnetic splitting of the $\frac{1}{2}+$ excited state into two sublevels and the quadrupole splitting of the $\frac{3}{2}+$ ground state into two sublevels. The ratio of the g factors of the excited state and the ground state is known from the measurements with the $Fe_{0.99}Ir_{0.01}$ absorber. The quadrupole splitting of the ground state is known from measurements above the Curie point of the various compounds. From the analysis of the spectrum with the highest effective field at the Ir nucleus ($GdIr_2$ at 20°K), it is clear that for all the spectra obtained $g_1\mu_nH_{\text{eff}}$ is small compared to $eqQ_1/4$. The relative separations between the sublevels of the ground level and the 73-keV level in $GdIr_2$ are shown in Fig. 7. It is clear from Fig. 7 why only four resolved lines are obtained in the split spectra. The magnetic splitting of the ground state is not resolved in the Mössbauer spectra and each of the resolved lines corresponds to two transitions between the sublevels which differ only slightly in energy. As long as $g_1\mu_nH_{\text{eff}}$ is small compared to $eqQ_1/4$, the distance between the first and the second absorption lines and the distance between the third and fourth absorption lines are proportional to H_{eff} for any fixed value of θ. The ratio between these distances in the various compounds is, therefore, a good measure of the ratio of the effective fields acting on the Ir nuclei in the various compounds. The four well-resolved lines obtained indicate that the effective fields in the different sites do not differ by more than 10%.

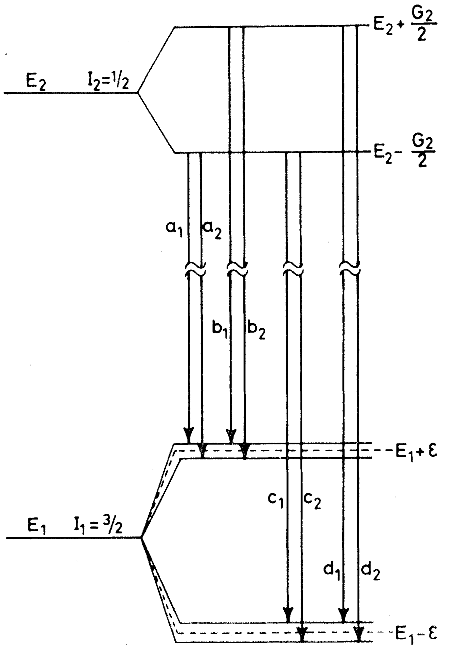

FIG. 7. The hyperfine splittings of the ground state and first excited state of Ir^{193} in $GdIr_2$ and the transitions between various substates.

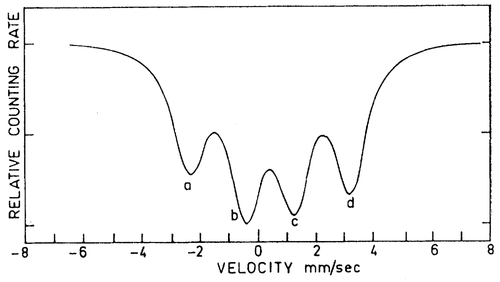

FIG. 8. Reconstructed recoilless absorption spectrum, assuming $g_2/g_1 = 9.1$, $g_2\mu_nH_{\text{eff}} = 122$ Mc/sec, $eqQ_1/4 = 106$ Mc/sec with two sites populated in the ratio 3:1; the first site with $\theta = 70°32'$ and the second with $\theta = 0°$ (see text).

We have tried to analyze the spectra more accurately by calculating the spectra expected theoretically as a function of H_{eff} and θ. The system of coordinates was chosen in such a way that the direction of the axis of the electric field gradients coincided with the z axis and H_{eff} was in the x, z plane. Then, the Hamiltonian of the hyperfine interactions of the $\frac{3}{2}+$ nuclear ground state is

$$\mathcal{H}_1 = g_1\mu_n(H_xI_{1,x} + H_zI_{1,z}) + [eqQ_1/4I_1(2I_1-1)] \times [3I_{1,z}^2 - I_1(I_1+1)]$$

and that of the $\frac{1}{2}+$ excited level is $\mathcal{H}_2 = g_2\mu_n(H_xI_{2,x} + H_zI_{2,z})$. By diagonalizing the corresponding matrices, the energies and the wave functions of the sublevels were calculated. Taking into account the value of $E2/M1$ derived from the measurements with the $Ir_{0.01}Fe_{0.99}$ absorber, the relative intensities of the eight transitions between the sublevels were calculated and the theoretical spectra reconstructed. Such spectra were calculated for $\theta = 70°\ 32'$ and various values of H_{eff} and also for a superposition of two spectra, one with $\theta = 70°\ 32'$ and a relative weight 3 and the second with $\theta = 0°$ and a relative weight 1. Figure 8 shows such a reconstructed spectrum assuming the same absolute value of $g_2\mu_nH_{\text{eff}} = 122$ Mc/sec for the two sites. The spectrum of Fig. 8 is very similar in shape to that obtained experimentally for $TbIr_2$ at 4.2°K (Fig. 5). Reconstructed spectra including a contribution from a site with $\theta = 0°$ (with a relative weight of 1:3) did not differ noticeably from those calculated for one site with $\theta = 70°\ 34'$, as long as the values of H_{eff} were assumed not to differ by more than 10% in the two sites. By comparing the experimental and the theoretical spectra, values of $g_2\mu_nH_{\text{eff}}$ in the various compounds could be derived. The relative values obtained in this way

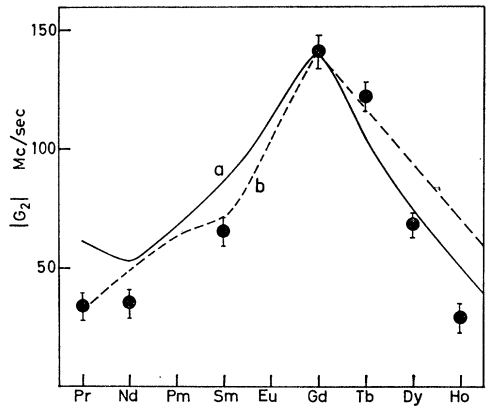

FIG. 9. The dependence of $|G_2|=|g_2\mu_n H_{\mathrm{eff}}|$ in $R\mathrm{Ir}_2$ compounds, on the atomic number (Z) of the rare-earth ion in the compound.

agreed very well with those derived from the simpler analysis described above.

The values of H_{eff} for PrIr_2, NdIr_2, and HoIr_2 were deduced from a comparison between the widths of the two broad lines obtained at 4.2°K and the widths of the lines in theoretically reconstructed spectra. The values of $|G_2|=|g_2\mu_n H_{\mathrm{eff}}|$ and $|H_{\mathrm{eff}}|$ found for the various intermetallic compounds are summarized in Table I. The values of $|G_2|$ for the various $R\mathrm{Ir}_2$ compounds are plotted in Fig. 9 as a function of Z. It should be emphasized that the sign of H_{eff} is not determined from the present measurements.

In Fig. 10 the temperature dependence of $|G_2|$ at the Ir nuclei in GdIr_2 is shown.

D. Iridium Salts

Mössbauer measurements were carried out at 4.2°K for the following Ir salts: IrI_3, $\mathrm{K_3IrCl_6}$, IrO_2, $\mathrm{K_2IrCl_6}$, and $\mathrm{(NH_4)_2IrCl_6}$. The spectra obtained in these measurements are shown in Figs. 11 and 12. The isomer shifts in these compounds relative to the source are summarized in Table II. Some previous results obtained by others[9] are also included in the table. The point symmetry of the Ir ions in $\mathrm{K_2IrCl_6}$ and in $\mathrm{(NH_4)_2IrCl_6}$ is cubic and the absorption spectra in them are not broadened by quadrupole interactions. The spectrum of IrO_2 consists of two resolved lines which arise from the quadrupole splitting of the $\frac{3}{2}+$ ground state. Each of the two lines is relatively broad. This broadening may indicate the existence of internal magnetic fields at the Ir nuclei, which are not completely cancelled to

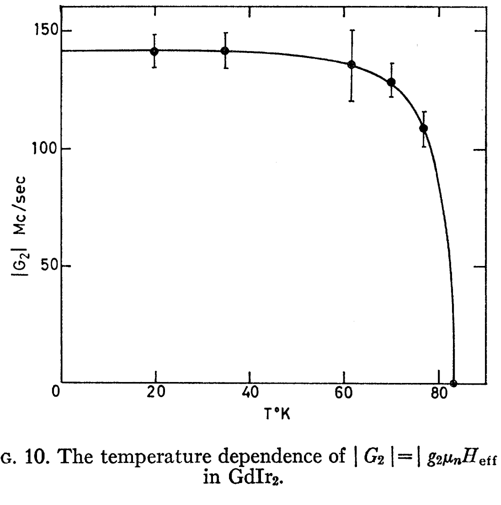

FIG. 10. The temperature dependence of $|G_2|=|g_2\mu_n H_{\mathrm{eff}}|$ in GdIr_2.

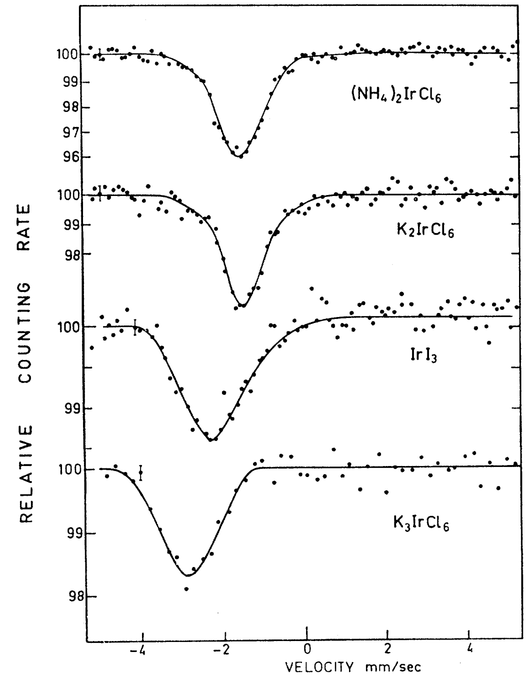

FIG. 11. Recoilless absorption by Ir tetravalent $[\mathrm{(NH_4)_2IrCl_6}$ and $\mathrm{K_2IrCl_6}]$ and trivalent $[\mathrm{IrI_3}$ and $\mathrm{K_3IrCl_6}]$ salts of the 73-keV γ rays of Ir^{193} as a function of relative velocity between source and absorber.

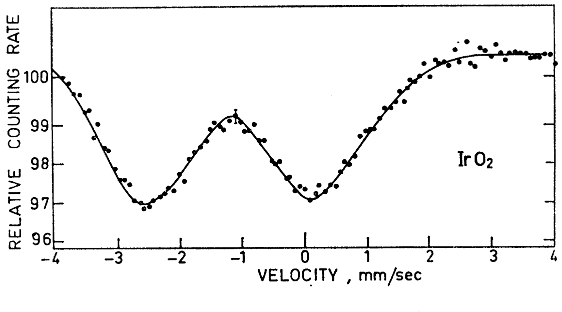

FIG. 12. Recoilless absorption by IrO_2 of the 73-keV γ rays of Ir^{193} as a function of relative velocity between source and absorber.

zero by relaxation phenomena. The broadening of the absorption spectra of IrI_3 and K_3IrCl_6 is very probably due to quadrupole interactions. The quadrupole interaction parameters $(eqQ_1/4)$ derived from the present measurements are summarized in Table II. (The parameters given for IrI_3 and K_3IrCl_6 were calculated assuming that the broadenings of the lines results from the quadrupole interactions only.)

DISCUSSION

A. The Nuclear Results

The present measurements confirm very definitely the assignment of spin $\frac{1}{2}$ to the 73-keV level and yield a value of 0.47 ± 0.03 nm for the magnetic moment of this level. According to the shell model, the ground level of the Ir^{193} nucleus is a $d_{3/2}$ level. The magnetic moment of the ground state is close to the Schmidt value of 0.124 nm. As the spin and parity of the 73-keV level is $\frac{1}{2}+$, the only possible single proton state assignment to it is $s_{1/2}$. The Schmidt value for the magnetic moment of such a level is 2.79 nm, which is much higher than the experimental value.

A small magnetic moment has also been found, by Grant *et al.*,[22] for the first excited 77-keV $\frac{1}{2}+$ level of Au^{197} $[\mu=(0.37\pm0.04)$ nm$]$. The structure of the levels of Au^{197} is very similar to that of Ir^{193}. The spin of the ground level is $\frac{3}{2}+$ and its magnetic moment is 0.136 nm. Braunstein and de Shalit[15,16] explained the properties of some of the excited levels of Au^{197} by assuming that they are produced by the coupling of the first excited $2+$ level of the Pt^{196} core with the $d_{3/2}$ level of the odd proton. Such a coupling results in a quadruplet of levels with spins $\frac{1}{2}+$, $\frac{3}{2}+$, $\frac{5}{2}+$, and $\frac{7}{2}+$. The 77-keV $\frac{1}{2}+$, the 268-keV $\frac{3}{2}+$, the 279-keV $\frac{5}{2}+$, and the 548-keV $\frac{7}{2}+$ levels of Au^{197} are identified by Braunstein and de Shalit as belonging to this quadruplet. If we assume that the same model also applies to Ir^{193}, the predicted magnetic moment of the 73-keV $\frac{1}{2}+$ level should be about 0.60 nm, in fair agreement with the present results. In Ir^{193}, there is a $\frac{1}{2}+$ level at 73 keV, a $\frac{5}{2}+$ level at 139-keV, and a $\frac{7}{2}+$ level at 362 keV. A $\frac{3}{2}+$ level was not identified until recently, but Avida and Burde,[23] who measured the decay scheme of Ir^{193} by coincidence and angular correlation techniques, using a Li-drifted Ge detector, came to the conclusion that Ir^{193} has a $\frac{3}{2}+$ level at 180 keV which decays predominantly to the $\frac{1}{2}+$ 73-keV level, as is the case in Au^{197}. Braunstein and de Shalit's core-excitation model explains the forbiddeness of transitions from the $\frac{3}{2}+$ excited state to the ground state.

TABLE II. Isomer shifts (ΔE) and quadrupole interaction constants (ϵ_1) in Ir compounds.

Compound	ΔE (mm/sec)	ϵ_1 (Mc/sec)
MIr_2	$0.3\ \pm0.1$	106 ± 4
$Ir_{0.01}Fe_{0.99}$	0.35 ± 0.05	0 ± 4
Ir metal	-0.55 ± 0.05	
	$-0.6\ \pm0.1^a$	
IrO_2	$-1.2\ \pm0.1$	80 ± 4
	$-1.4\ \pm0.2^a$	70 ± 6^a
K_2IrCl_6	-1.45 ± 0.05	0 ± 4
	$-1.7\ \pm0.2^a$	
$IrCl_4$	$-1.4\ \pm0.3^a$	
$(NH_4)_2IrCl_6$	-1.45 ± 0.05	6 ± 6
IrI_3	-2.20 ± 0.05	21 ± 4
K_3IrCl_6	-2.85 ± 0.10	18 ± 4
$IrCl_3$	-2.5^b	

[a] Reference 9.

[b] P. Kienle *et al.* (private communication).

B. Isomer Shifts

The isomer shifts obtained between the various absorbers used and the Ir and Os metal source are summarized in Table II. From the table it is seen that the isomer shifts of the tetravalent Ir compounds $[IrO_2$, K_2IrCl_6, $(NH_4)_2IrCl_6$, and $IrCl_4]$ relative to the trivalent Ir compounds (IrI_3, K_3IrCl_6, and $IrCl_3$) are positive. The electronic configuration of the Ir atom is $[Xe]\ 4f^{14}\ 5d^7\ 6s^2$, that of Ir^{3+} is $[Xe]\ 4f^{14}\ 5d^6$, and that of Ir^{4+} is $[Xe]\ 4f^{14}\ 5d^5$. It is very reasonable to assume that in tetravalent Ir compounds, the d electrons shield less effectively the external s electrons than in the trivalent Ir compounds and that the s electron density $\psi_s^2(0)$ at the Ir nucleus in the tetravalent compounds is larger than in the trivalent compounds. The conclusion is therefore that the sign of $\Delta\langle r^2\rangle$, the difference in the mean-square radius of the charge distribution between the 73-keV level and the ground level of Ir^{193}, is positive.

The isomer shift of Ir metal is ~1.9 mm/sec relative to the trivalent compounds and ~0.9 mm/sec relative to the tetravalent compounds. An accurate estimate of $\Delta\psi_s^2(0)$ between Ir metal and Ir salts requires at least a knowledge of (1) the degree of covalent bonding as well as its effects on the s wave function density for the Ir salts and (2) the number of effective $6s$ electrons in Ir metal. None of this information is really known. We assume, for the purpose of getting a very rough estimate of $\Delta r/r$, that the Ir salts are 100% ionic, that Ir metal is trivalent, and that the contribution of the conduction electrons to $\psi_s^2(0)$ is equivalent to that of one effective $6s$ electron. [In the trivalent rare-earth metals, in metallic iron, and in tin the contribution of the conduction electrons to $\psi_s^2(0)$ also equals that of one outer

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[22] R. W. Grant, M. Kaplan, D. A. Keller, and D. A. Shirley, Phys. Rev. **133**, A1062 (1964).

[23] R. Avida and J. Burde (private communication).

electron.[24,25]] Using these assumptions, we obtain a value of about 6×10^{26} cm^{-3} for $\psi_s^2(0)$ and a value of 6×10^{-5} for $\Delta r/r$. Grant *et al.*[22] deduced a value of $\Delta r/r=2.10^{-4}$ for the first excited level of Au^{197}, from isomer-shift measurements on Au as impurity in various metals. As explained above, the structure and properties of the levels in Ir^{193} and in Au^{197} are very similar. Because of the crudeness of the estimates of the electron densities in the analysis of the Ir^{193} and Au^{197} measurements, it is difficult to be sure whether the difference between the quoted results for $\Delta r/r$ between Ir^{193} and Au^{197} is real.

The isomer shifts obtained for all the RIr$_2$ compounds are the same within the experimental errors. These shifts are positive with respect to Ir metal, indicating a larger s-electron density at the Ir^{193} nuclei in these compounds than in Ir metal. Previous isomer-shift measurements on the 26-keV γ rays of Dy^{161} have shown that the isomer shift between DyIr$_2$ and Dy^{3+} salts (0.3 ± 0.1 mm/sec) is much smaller than the shift between Dy metal and the Dy^{3+} salts (1.9 ± 0.1 mm/sec).[26] These results tend to show that there is a transfer of the conduction electrons in the RIr$_2$ compounds from the rare-earth ions towards the Ir ions. White *et al.* have arrived at similar conclusions for the RAl$_2$ compounds.[27] They carried out susceptibility measurements on the system Ce$_x$La$_{1-x}$Al$_2$ and concluded that their results can be explained if it is assumed that the conduction electrons concentrate at the aluminum sites in these metals at the expense of the rare-earth ion sites.

C. H_{eff} at the Ir Nuclei in the RIr$_2$ Intermetallic Compounds

Previous Mössbauer-effect measurements have shown that the value of H_{eff} at the Dy nuclei in DyIr$_2$ at 4.2°K is very close to the free-ion value,[26] indicating that the Dy ion is completely magnetized and its moment is very close to the free-ion value of 10 μ_B. The same is very probably true for the other MIr$_2$ compounds at low temperatures. Bulk magnetization measurements were previously interpreted as showing that the moments of the rare-earth ions in the RIr$_2$ compounds are considerably smaller than the free-ion values,[1] but as explained in Ref. 26, the Mössbauer-effect measurements are not consistent with these interpretations. The magnetization measurements can be explained by assuming that the domains were not completely oriented.

We have tried to analyze our results for the dependence of H_{eff} on R, (the rare-earth ion in the RIr$_2$ compound) by assuming that the fields at the Ir nuclei are produced by the s conduction electrons, which are polarized by their interactions with the $4f$ electrons of the rare-earth ions (s-f interaction). The polarized s conduction electrons contribute to H_{eff} mainly through the following two mechanisms: (1) A direct contribution through the Fermi contact interaction; (2) an indirect contribution of the non-s conduction electrons polarized by the s conduction electrons and of the Ir core electrons polarized by the conduction electrons. Both these contributions to H_{eff} are expected to be proportional to the polarization of the s conduction electrons.

According to the Kasuya-Yosida model,[5,6] the polarization of the conduction electrons at a diamagnetic ion is given by

$$P=(-9\pi Z/E_F)\Gamma(g_J-1)\sum_n[F(2\mathbf{k}_F\cdot\mathbf{R}_n)\langle J_z\rangle_n],\quad(1)$$

where Z is the number of conduction electrons per rare-earth ion, E_F is the Fermi energy, Γ is the s-f coupling constant, F is the oscillating Ruderman-Kittel function, $\mathbf{k}_F$ is the Fermi momentum, and $\mathbf{R}_n$ is the distance of a rare-earth ion from the diamagnetic ion. The summation is carried out over all rare-earth ions. The sum $\sum_n F_n$ is expected to have, very closely, the same value for all the RIr$_2$ compounds. If it is assumed that Z, E_f, and Γ are the same for all the RIr$_2$ compounds investigated, then P and H_{eff} should be proportional, at magnetic saturation, to $(g_J-1)J$. In Fig. 13, the experimental values of $|g_2\mu_n H_{\text{eff}}|$ at 4.2°K are given as a function of $(g_J-1)J$. According to the simple assumptions made above, the points should lie on the solid lines in the figure. It is seen that the points corresponding to positive values of $(g_J-1)J$ do not lie on the theoretical line but on the dashed line which intersects the abscissa at $(g_J-1)J=\sim1.5$. Very similar relations between H_{eff} and $(g_J-1)J$ for the heavy rare-earth ions (Gd and above) were previously observed by Bosch *et al.*[3] for Sn in the rare-earth metals and in the R_2Sn intermetallic compounds and by Cohen *et al.*[2] for Hf in the rare-earth metals. Some of these results are also shown in Fig. 13. Bosch *et al.* have pointed out that it was possible to interpret their results for Sn in rare-earth metals by

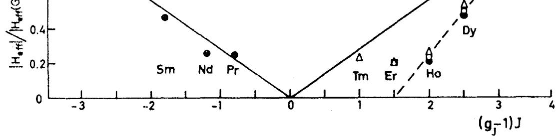

FIG. 13. The dependence of $|G_2|=|g_2\mu_n H_{\text{eff}}|$ on the value of $(g_J-1)J$ of the rare-earth ion. Points represent the present results for Ir in the RIr$_2$ compounds. Triangles represent results for Sn in the rare earth metals (Ref. 3). Squares represent results for Sm in R_2 Sn compounds (Ref. 3).

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[24] P. Brix, S. Hufner, P. Kienle, and D. Quitmann, Phys. Letters **13**, 140 (1964).

[25] D. A. Shirley, Rev. Mod. Phys. **36**, 339 (1964).

[26] I. Nowik, S. Ofer, and J. H. Wernick, Phys. Letters **20**, 232 (1966).

[27] J. A. White, H. J. Williams, J. H. Wernick, and R. C. Sherwood, Phys. Rev. **131**, 1039 (1963).

assuming that H_{eff} is a sum of two terms, one of them proportional to $(g_J-1)J$ and the other to g_JJ which is roughly constant for all the heavy rare-earth ions which have been investigated.[3] The present measurements for the lighter rare-earth ions in the $R\mathrm{Ir}_2$ compounds are not consistent with this interpretation, according to which the values of $H_{\mathrm{eff}}(R\mathrm{Ir}_2)/H_{\mathrm{eff}}(\mathrm{GdIr}_2)$ for Sm, Nd, and Pr should be about 1.0, 0.9, and 0.7, respectively. The corresponding experimental values are 0.46, 0.25, and 0.24. It should be emphasized that the group of the rare-earth metals is not a simple system for the purpose of checking the validity of theories about the polarization of the conduction electrons. As the magnetic ordering of Ho, Er, and Tm is quite complex at 4.2°K the value of $\langle J_z\rangle$ is not the same for all the ions in the metal and the sums $\sum_n[F_n\langle J_z\rangle_n]$ appearing in Eq. (1) cannot be expressed in the form $J\sum_nF_n$. The conclusion is therefore that even if we assume that the values of Z, E_F, and Γ are the same for all the rare-earth metals, P is not necessarily expected to be proportional to $(g_J-1)J$ for all of them. Nevertheless, as stated above, the results for the heavier rare-earth elements look surprisingly similar for various diamagnetic impurities in the pure metals and for the intermetallic compounds which have been investigated.

Somewhat better agreement between the present experimental results for the heavy rare-earth ions and the Kasuya-Yosida model is obtained if it is not assumed that the s-f coupling constant Γ has the same value for all the $R\mathrm{Ir}_2$ compounds. Changes of Γ throughout the rare-earth series were observed in Knight-shift measurements on $R\mathrm{Al}_2$ compounds and in some EPR measurements and have been explained theoretically by considering interband mixing between the conduction and local moment electron orbitals by Watson *et al.*[28] According to de Gennes,[29] the paramagnetic Curie temperatures θ_p of the $R\mathrm{Ir}_2$ compounds are given by the formula

$$k\theta_p=(-3\pi Z^2/4E_F)\Gamma^2(g_J-1)^2J(J+1)\sum_n \mathrm{F}(2\mathbf{k}_F\cdot\mathbf{R}_n). \tag{2}$$

The summation is over all the rare-earth ions, taking one of them as the origin (not including the one at the origin). No experimental values for the paramagnetic Curie temperatures θ_p of the $R\mathrm{Ir}_2$ compounds are available, but their ferromagnetic transition temperatures θ_f were measured by Bozorth *et al.*[1] and found to be correlated with the de Gennes factor of $J(J+1)(g_J-1)^2$ but not exactly proportional to it. The relative values of the polarizations of the conduction electrons can be calculated from the measured values of θ_f and Eq. (1) by making the following assumptions: (1) The ratio of the paramagnetic transition temperatures θ_p for any two $R\mathrm{Ir}_2$ compounds is equal to the ratio of their ferromagnetic transition temperatures θ_f. (2) E_F is the same for all the $R\mathrm{Ir}_2$ compounds. Under these assumptions, the polarization of the conduction electrons in the $R\mathrm{Ir}_2$ compounds is given by

$$P=a[\theta_fJ/(J+1)]^{1/2}, \tag{3}$$

where a is a constant for all the $R\mathrm{Ir}_2$ compounds.

In Fig. 9 the experimental relative values of $|H_{\mathrm{eff}}|$ at the Ir nuclei in the $R\mathrm{Ir}_2$ compounds are compared to the relative values calculated from Eq. (3) [curve (a)] and with the relative values calculated assuming that the conduction-electron polarization is proportional to $(g_J-1)J$ [curve (b)]. It is seen that the experimental ratios for the heavy rare-earth ions are in somewhat better agreement with curve (a) than with curve (b). The Curie temperature of HoIr_2 is 12°K and it is possible that H_{eff} did not reach its maximum value at 4.2°K. The fact that the relative values of $|H_{\mathrm{eff}}|$ are approximately equal to the theoretical relative values of the conduction-electron polarizations increases somewhat the confidence in the assumption that H_{eff} is produced mainly through processes whose primary sources are the polarized s conduction electrons. Taking into account the crudeness of the theory it is hard to expect any better fit of the experimental points to the theoretical lines.

In the present experimental results, the signs of H_{eff} were not determined. For Sn in Gd metal, Bosch *et al.* found a positive value for H_{eff}.[3] For Lu and Hf in Gd metal, Cohen *et al.* found H_{eff} to be negative.[2] The sign of the polarization of the conduction electrons is expected to be the same for the two cases and the difference in the sign of H_{eff} can be explained by assuming that the two contributions to H_{eff} (direct Fermi contact interaction and core polarization) have opposite signs and that the sign of their sum for Sn is opposite to that for Lu and Hf.

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[28] R. E. Watson, S. Koide, M. Peter, and A. J. Freeman, Phys. Rev. **139**, A167 (1965).

[29] P. G. de Gennes, J. Phys. Radium **23**, 510 (1962).