

Nuclear-Quadrupole Interactions in Perovskite-Type Compounds of Hf¹⁸¹ Studied by the Perturbed-Angular-Correlation Technique*

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(Received 15 December 1971)

Measurements of nuclear-quadrupole-interaction constants in perovskite-type compounds of PbHfO₃, SnHfO₃, CaHfO₃, and SrHfO₃ have been performed using the perturbed-angular-correlation technique. A range of fundamental frequencies from 150×10^6 to 550×10^6 rad/sec was determined. The variation of the quadrupole constants has been discussed through the molecular-orbital theory. A semiempirical formula for the admixture coefficient between d wave functions and p wave functions which describes the covalent bonding present in each ABO₃ compound has been derived.

INTRODUCTION

The perturbed-angular-correlation (PAC) technique has previously been used successfully¹⁻⁷ to determine nuclear-quadrupole-interaction constants in several compounds of Hf¹⁸¹. Compounds of low oxidation states such as HfO₂, HfOCl₂·8H₂O, Hf metal, ZrHf, as well as of high oxidation states such as (NH₄)₂HfF₆ and (NH₄)₃HfF₇, have been studied through the perturbation of the angular correlation in the $\frac{1}{2} \rightarrow \frac{5}{2} \rightarrow \frac{7}{2}$ cascade with γ energies of 133 and 482 keV of Ta¹⁸¹, where the intermediate state has a lifetime $\tau_N = 15.8$ nsec. One of the main features of these studies was that even in the case when the decaying nucleus is surrounded by an octahedron of ions and it has an apparent electronic configuration d^0 , as in (NH₄)₂HfF₆, a quadrupole interaction was found.⁵ Owing to this fact it seemed interesting to investigate more compounds in which the decaying nucleus has an apparent electronic configuration d^0 and an octahedral environment. Good examples of such compounds are the compounds of perovskite-type structure ($A^{2+}B^{4+}O_3$).

In this paper we report measurements of nuclear-quadrupole-interaction constants in the perovskite-type compounds PbHfO₃, SnHfO₃, CaHfO₃, and SrHfO₃ containing radioactive Hf¹⁸¹. The interpretation of the electric field gradients (EFG) due to effects of covalent bonding is considered.

METHODS AND APPARATUS

The angular-correlation function, describing the coincidence counting rate of two successive radiations emitted in relative directions given by an angle θ and separated by a time interval t during which a perturbation acts on the intermediate state, can be written for the case of a liquid or a polycrystalline powder source as¹

$$W(\theta, t) = \sum_k A_k(1) A_k(2) G_{kk}(t) P_k(\cos\theta), \quad (1)$$

where $A_k(1)$ and $A_k(2)$ are the usual angular-corre-

lation coefficients and $G_{kk}(t)$ is the perturbation factor. For static quadrupole interactions the perturbation factor $G_{kk}(t)$ has the form¹

$$G_{kk}(t) = \sum_n S_{kn} \cos(\omega_n t), \quad (2)$$

where the factors S_{kn} depend on the state n involved and the asymmetry parameter η of the EFG. Detailed formulas are given in Ref. 1.

An expression for the perturbation factor including simultaneous static and time-dependent quadrupole interactions is given in Ref. 8. Effects on the perturbation factor due to a Gaussian distribution of frequencies arising from an inhomogeneous EFG are described in Ref. 9.

The behavior of the perturbation factor $G_{kk}(t)$ as a function of time was measured with a coincidence system consisting basically of a time-to-pulse-height converter and a 512-channel analyzer. The detectors were a 6810-A photomultiplier with a $2 \times 1\frac{1}{2}$ -in. -diam NaI(Tl) crystal for the high-energy γ and a XP-1021 with a $1 \times 1\frac{1}{2}$ -in. -diam NaI(Tl) crystal for the low-energy γ . The total time range in the differential measurement was 100 nsec and the full width at half-maximum of the prompt peak, taken with Na²² with the energy settings for the Ta¹⁸¹ cascade, was 2.4 nsec in all measurements. The equipment was tested by the measurement of the known quadrupole interaction in Hf metal. Time spectra were accumulated in the multichannel analyzer for relative angles between the detectors of 90°, 180°, and 270°. All the sources were prepared by heating stoichiometric mixtures of hydrated oxide of Hf¹⁸¹ and carbonates of the corresponding elements. The mixtures were dried and calcinated at 1000 °C (for Pb and Sn compounds) and 1550 °C (for Ca and Sr compounds).

RESULTS AND DATA TREATMENT

The results of the differential measurements made on the polycrystalline sources PbHfO₃, SnHfO₃, CaHfO₃, and SrHfO₃ are shown in Figs.

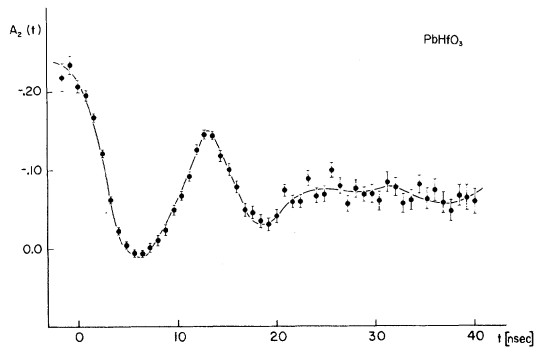


FIG. 1. Perturbation factor $A_2G_{22}(t)$ for the 133-482 keV γ - γ cascade of Hf^{181} measured in the compound PbHfO_3 . The solid line is a theoretical curve for the set of frequencies $(439, 542, 908) \times 10^6$ rad/sec, $\delta = 11.5\%$, and $\eta = 0.75$.

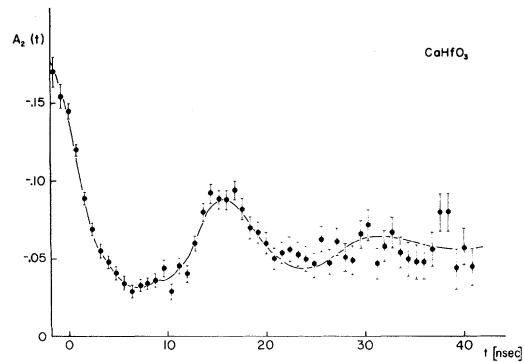


FIG. 3. Perturbation factor $A_2G_{22}(t)$ for the 133-482 keV γ - γ cascade of Hf^{181} measured in the compound CaHfO_3 . The solid line is a theoretical curve for the set of frequencies $(362, 739, 1152) \times 10^6$ rad/sec and $\delta = 15.3\%$.

1, 2, 3, and 4, respectively. The behavior of the experimental curves for PbHfO_3 and CaHfO_3 [given by $A_2(t) = A_2G_{22}(t)$] shows a strong decrease of amplitude of the resonance peak with time. The solid line is a fitted theoretical curve obtained through

$$G_k(t, \delta) = \sigma_0 + \sum_n \sigma_{kn} \exp(-\frac{1}{2} \omega_n^2 \delta^2 t^2) \cos \omega_n t$$

for a set of frequencies plus a distribution of frequencies δ for each case. The large frequency distribution which is seen in the experimental curve led us to suspect that more subfrequencies were involved due either to other sublattices or to a mixture of different compounds.

It is known¹⁰ that compounds of $A^{2+}B^{4+}O_3$ usually have a mixture of BO_2 . Analysis of x-ray patterns of nonradioactive samples produced in the same way as the radioactive sources demonstrated in fact the existence of HfO_2 in our case.

In order to separate the quadrupole interactions involved we have treated the data by a method which combines Fourier analysis and nonlinear least-

squares techniques as described in Ref. 11. The method consists basically of the following procedures, which we have used: (a) The finite Fourier transform of the experimental $G_{22}(t)$ was taken. (b) The Fourier transform of the time resolution was determined from the measured $A_0(t)$ and the experimentally known lifetime. This technique has the advantage of using the same data to determine the experimental prompt time resolution and the attenuation coefficient $G_{22}(t)$. (c) The Fourier transform of the measured spectrum was then divided by the transform of the resolution function giving the transform of the "unfolded" function. A cutoff frequency was chosen above which the transform of the unfolded function was set to zero in order to avoid magnifying the effects of the noise spectrum at high frequencies. (d) The inverse transform of the "unfolded" spectrum was then taken, resulting in a reconstructed "experimental" spectrum free from the effects of finite time reso-

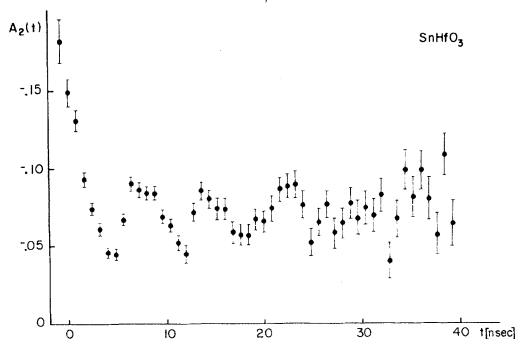


FIG. 2. Perturbation factor $A_2G_{22}(t)$ for the 133-482 keV γ - γ cascade of Hf^{181} measured in the compound SnHfO_3 .

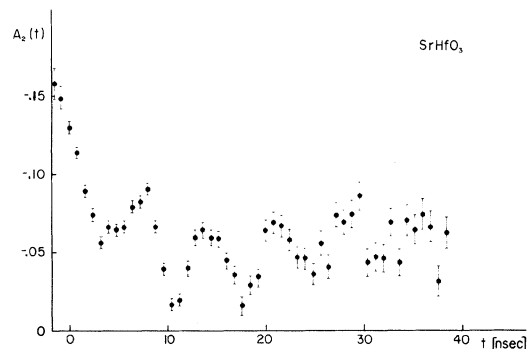


FIG. 4. Perturbation factor $A_2G_{22}(t)$ for the 133-482 keV γ - γ cascade of Hf^{181} measured in the compound SrHfO_3 .

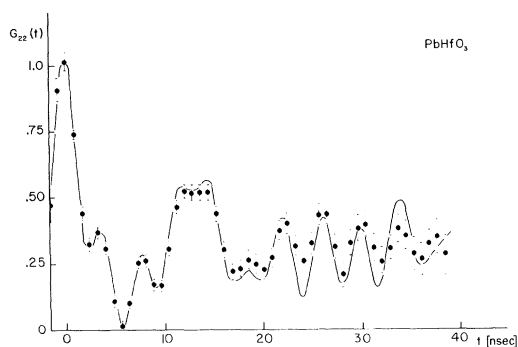


FIG. 5. Reconstructed experimental spectrum of $G_{22}(t)$ for the compound PbHfO_3 . The solid line results from a nonlinear least-squares fit using two sets of frequencies.

lution. (e) Finally, an analytic nonlinear least-squares fit was made to the data using fitting functions of the type

$$T(t) = \sum_i A_i \cos \omega_i(t - t_0) + B$$

to obtain the best values of the frequencies and amplitudes involved. The reconstructed curves using this procedure are shown in Figs. 5, 6, 7, and 8 for PbHfO_3 , SnHfO_3 , CaHfO_3 , and SrHfO_3 , respectively. Details of this treatment can be found in Ref. 11. The curves were fitted with the frequency sets given in Table I.

DISCUSSION AND CONCLUSIONS

From Table I it is seen that the second set of frequencies in all compounds of the type $A^{2+}B^{4+}O_3$ measured can be considered as due to the presence of HfO_2 (with electronic configuration d^1 for Ta^{181}), since the quadrupole interaction in this compound is well known^{3, 4} and is of this order of magnitude.

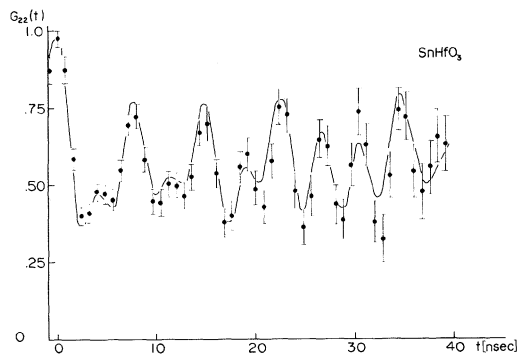


FIG. 6. Reconstructed experimental spectrum of $G_{22}(t)$ for the compound SnHfO_3 . The solid line results from a nonlinear least-squares fit using two sets of frequencies.

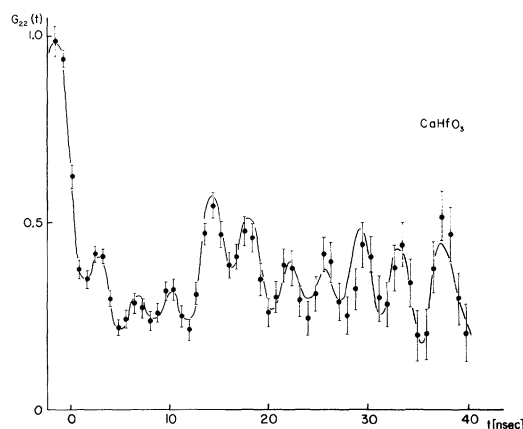


FIG. 7. Reconstructed experimental spectrum of $G_{22}(t)$ for the compound CaHfO_3 . The solid line results from a nonlinear least-squares fit using two sets of frequencies.

From the way the compounds were prepared there exists a fraction of HfO_2 in the samples. Thus we can simply assume that all first sets of frequencies correspond to the nuclear-quadrupole interaction due to the ABO_3 compounds themselves.

Using the procedure described in Refs. 5 and 12, we can derive values for the EFG's using the lowest frequencies of the first sets as the fundamental frequencies. The quadrupole moment is known¹³ to be $Q = (2.51 \pm 0.10)10^{-24} \text{ cm}^2$ for the intermediate level with $I = \frac{5}{2}$. The values so obtained are summarized in Table II together with some information from Ref. 14 on the structure of these compounds at room temperature.

From Table II one sees that we have two groups of ABO_3 compounds: (a) one in which A has an electronic configuration s^2 and (b) one in which A has the electronic configuration s^2p^2 . One sees that the EFG's of the group s^2p^2 are larger than

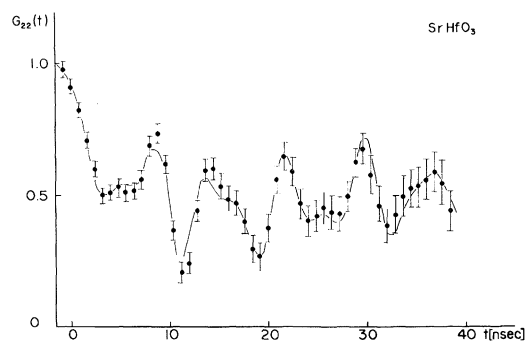


FIG. 8. Reconstructed experimental spectrum of $G_{22}(t)$ for the compound SrHfO_3 . The solid line results from a nonlinear least-squares fit using two sets of frequencies.

TABLE I. Sets of frequencies in 10^6 rad/sec obtained from Fourier analysis of experimental perturbation factor $A_2G_{22}(t)$ for each ABO_3 compound.

	CaHfO ₃	SrHfO ₃	SnHfO ₃	PbHfO ₃
First set of frequencies in 10^6 rad/sec	289	149	551	410
Second set of frequencies in 10^6 rad/sec	806	870	891	1470
	1640	1497	1658	1680

those of the group s^2 ; one also sees that within the same group the EFG decreases with increasing n .

The nuclear-quadrupole interaction is measured in Ta¹⁸¹ which originates from the decay of Hf¹⁸¹. From atomic spectroscopy, we know that the ground state for Ta¹⁸¹ is $^4F_{3/2}$ and the configuration of the outer electrons is $5d^3 6s^2$. Thus, due to the presence of a third d electron (Hf itself has the structure $5d^2 6s^2$), a new arrangement must occur in the chemical bonding. We can consider two extreme cases: (a') The previous bonding with Hf¹⁸¹ is unchanged and then the outer-electron configuration for Ta¹⁸¹ is d^1 , the outer electron being a localized one. (b') The bonding after the decay is changed, the electron configuration for Ta¹⁸¹ being d^0 .

The EFG's would have their extreme values for d^1 if a small distortion of cubic symmetry occurred,¹⁵ leaving a nondegenerate electronic ground state. The order of magnitude¹² of V_{zz} in this case will be the one measured in HfO₂, HfOCl₂·8H₂O. For d^0 they would vanish or be very small due to the distorted oxygen octahedra. Covalent effects¹⁶ can account for values of V_{zz} between these two extreme cases.

In order to discuss the observed variation of V_{zz} we follow the molecular-orbital theory given in Ref. 17 concerning the effects of covalent bonding

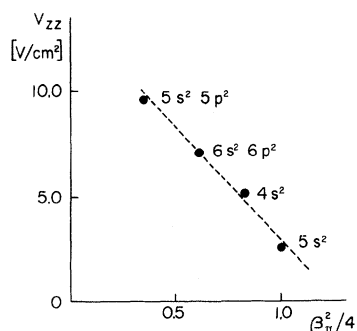


FIG. 9. Behavior of the EFG V_{zz} as a function of the factor $\beta_{\pi}^2/4$ for the four ABO_3 compounds. Derived values for V_{zz} are corrected by an asymmetry parameter.

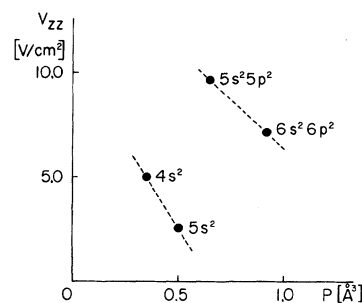


FIG. 10. Behavior of the EFG V_{zz} as a function of the polarizability of the ion A of the compounds ABO_3 studied.

on the magnetic properties of octahedrally coordinated ions with an unfilled d shell. An electrostatic potential produced by ions forming an octahedron splits the energy levels for d electronic wave functions. For d^1 , there is a splitting into two orbital sets e_g (twofold orbitally degenerate) and t_{2g} (threefold orbitally degenerate). The covalency is taken into account by admixing ligand s and p orbits into the central-ion d orbits in complexes of type MX_6 , where M is the central ion and X_6 is the surrounding octahedron of ligands. The molecular orbitals in an octahedral complex for one-electron d mixing with s and p orbits are given in Ref. 17. If a small distortion of the ligand octahedron occurs¹⁵ the molecular ground state is given by

$$\Psi_{xy} = N_{\pi} [d_{xy} - \frac{1}{2}\alpha_{\pi}(y_1 - y_4 + x_2 - x_5)], \quad (3)$$

where x , y , and z represent the p orbitals from the outer shell of the ligand. The numbers refer to ligands on the x , y , z , $-x$, $-y$, $-z$ axes of the octahedron; the s orbitals hybridize with the w wave function from the set e_g . The normalization constant for a π bonding (hybridization of t_{2g} set with p orbitals) is given by $N_{\pi}^{-2} = 1 - 4\alpha_{\pi} s_{\pi} + \alpha_{\pi}^2$, $s_{\pi} = \langle d_{xy} | y_1 \rangle$ being the overlap integral.

With this molecular wave function we can calculate the EFG $\langle \Psi_{xy} | V_{zz} | \Psi_{xy} \rangle$, where V_{zz} is the field gradient operator. After some calculations, neglecting cross terms, one obtains

TABLE II. EFG's derived for the ABO_3 compounds.

ABO_3	Outer electron configuration of A	Structure at room temperature	Polarizability of A	Derived value of V_{zz} in 10^{11} V/cm ²
CaHfO ₃	$4s^2$	Cubic or pseudocubic	0.35	3.80
SrHfO ₃	$5s^2$	Cubic or pseudocubic	0.50	2.32
SnHfO ₃	$5s^2 5p^2$	Cubic or pseudocubic	0.65	6.96
PbHfO ₃	$6s^2 6p^2$	Orthorhombic	0.91	4.95

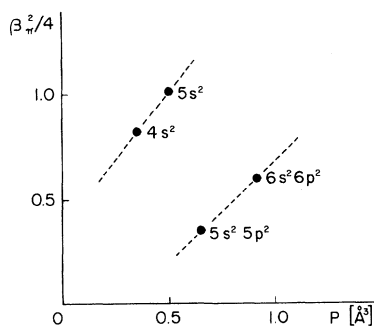


FIG. 11. Behavior of the factor β_r^2 as a function of the polarizability of the ion A of the compounds ABO_3 obtained from Figs. 9 and 10.

$$V_{zz} \approx N_r^2 \left(\frac{4}{7} e \langle r^{-3} \rangle_{n=5}^{Ta(d^1)} - \frac{12}{5} \frac{\beta_r^2}{4} e \right). \quad (4)$$

Using the value of $\langle r^{-3} \rangle$ tabulated in Ref. 18, one obtains as the final result

$$V_{zz} \approx 3.24 N_r^2 e - 2.40 N_r^2 \frac{\beta_r^2}{4} e, \quad (5)$$

which is an equation for the EFG as a function of the factor β_r^2 . This factor depends on the admixture factor α_r^2 and on an integral that takes into account the relationship between the two centers for the EFG. Such relationship can be obtained using Löwdin's α technique¹⁹ to expand the functions from one center to the other.

For our series of compounds this integral will be approximately a constant, and it will affect only the slope of our line. In this work, we are primarily interested in finding the trend of V_{zz} as a function of β_r^2 . From Eq. (5) we can derive a semi-empirical formula given by

$$\frac{\beta_r^2}{4} \approx \frac{N_r^2 V_{zz}(d^1)_{\text{theor}}}{N_r^2 V_{zz}(p)_{\text{theor}}} \left(1 - \frac{V_{zz}(ABO_3)_{\text{expt}}}{V_{zz}(BO_2)_{\text{expt}}} \right), \quad (6)$$

where the field gradient $V_{zz}(BO_2)$ is known to be 13×10^{17} V/cm² as it corresponds to an electronic configuration d^1 . Using the experimental values for V_{zz} given in Table II, one obtains the behavior of β_r^2 as shown in Fig. 9. One sees immediately that β_r^2 is a function of n and of the electronic density. Figure 10 shows the relationship between the derived EFG's and the polarizability of the ion A taken from Table II. Figure 11 shows the re-

lationship between the factor β_r^2 and the polarizability of the ion A . This relationship tells us that the delocalization of d^1 in compounds $AHfO_3$ (when Hf decays to Ta) is a function of the polarizability and of the mean radius $\langle r \rangle_n$ of the ion A . A further systematic study of the EFG as a function of temperature in compounds in this type can reveal new features of the relationship between the factor β_r^2 and polarizability of the ion A .

However, in the approach above, we have neglected the lattice contribution to the EFG. From Refs. 14 and 20, we obtained information that CaHfO_3 , SrHfO_3 , and SnHfO_3 are cubic or pseudocubic and that PbHfO_3 is orthorhombic. Using data from Ref. 20, we have calculated for PbHfO_3 the EFG due to the lattice through the method of lattice sums. It turned out to be $V_{zz}^{\text{lat}} \approx 0.24 \times 10^{17}$ V/cm² (including the amplification due to the Sternheimer factor ≈ 70), which is approximately 6% of the experimental value for V_{zz} . Unfortunately, we have not found detailed data on the remaining structures we studied, but it seems reasonable to assume that the lattice contribution will be small for all the cases. Even in the case where we assume a change of 30% in the lattice contribution, this variation will not explain the variation found for our series of ABO_3 .

In conclusion, we want to point out that this approach shows some features of the mechanism responsible for covalent effects in chemical bonding and, applied to suitable series of compounds, can indicate the extension of applicability of molecular-orbital theory to describe EFG's due to covalent effects. Moreover, studies as a function of temperature in a series of compounds of this type will elucidate the contribution of the lattice to the EFG, particularly in phases with different structures. The competition between covalency and structure change and how they are correlated are interesting points to be investigated.

ACKNOWLEDGMENTS

The authors thank the chemist E. R. Fraga for preparation of our chemical compounds and one of us (P. da R. A.) thanks P. J. Viccaro for interesting discussions concerning covalent effects. We thank also A. Vasquez for the program on lattice sums.

*Work partially supported by the International Atomic Energy Agency and the Brazilian organizations Conselho Nacional de Pesquisas, Banco Nacional de Desenvolvimento Econômico, Conselho de Pesquisas da Universidade Federal do Rio Grande do Sul, and Comissão Nacional de Energia Nuclear.

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Single-Passage Resonance Studies by β Emission and the Measurement of Spin-Lattice Relaxation Times for $Fe^{60}Co$

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 (Received 3 September 1971)

β -particle measurements of the signal produced during single- and multiple-passage nuclear magnetic resonance of oriented ^{60}Co nuclei in single crystals of iron are reported. Comparison of the signals from β^- and γ radiations shows that after single passages the changes in the orientation parameters are describable in terms of a rotation through a well-defined angle. This constitutes a known set of initial conditions for the subsequent relaxation back to equilibrium so that accurate values of the spin-lattice relaxation time T_1 can be obtained. A nonresonant method of measuring T_1 accurately is also described and is shown to give results in agreement with the single-passage technique. We obtain a value $K = 1.75 \pm 0.15$ sec K for $Fe^{60}Co$. This differs from values previously reported from experiments in which the initial conditions were not well known. Comparison of the β^- and γ signals after multiple passages show, as expected, that the changes in the orientation parameters are not then describable in terms of a single angle of rotation.

I. INTRODUCTION

The first observation of NMR on oriented nuclei in ferromagnets was reported by Matthias and Holiday.¹ In this technique the resonance is detected via the partial destruction of the anisotropic distribution of radiation emitted from statically oriented radioactive nuclei. Although considerable knowledge of the hyperfine parameters has been obtained, a complete understanding of the magnitude of the fractional reduction in radiation anisotropy is lacking. The problem is complex because the large inhomogeneous broadening in ferromagnets necessitates frequency modulation.² Also, at the very low temperatures necessary to orient nuclei and at the relatively high frequencies used, there are additional complications with eddy-

current heating and skin depth.

In a previous attempt to understand the problem, a theoretical and experimental study of single-passage NMR of ^{60}Co in Fe detected via γ radiation was reported.³ This single-passage approach affords a considerable theoretical simplification over the continuous-modulation procedure. However, even in this simpler case, a major discrepancy was observed between the angle of rotation of the nuclear ensemble as deduced from the observed single-passage signals and the angle of rotation calculated theoretically. It was tentatively postulated that the discrepancy might be caused by the effect of the nuclear polarization back onto the electrons.

In this paper we are not concerned with the cause of this discrepancy but rather with the application