PHYSICAL REVIEW B VOLUME 1, NUMBER 7 1 APRIL 1970

Nuclear Relaxation in $(NH_4)_3HfF_7$ Studied by Gamma-Gamma Angular Correlation*

P. DA R. ANDRADE, A. VASQUEZ, J. D. ROGERS, AND E. R. FRAGA
Instituto de Física, Universidade Federal do Rio Grande do Sul, Pôrto Alegre, RS, Brasil

(Received 8 September 1969)

Measurements of the perturbed angular correlation have been made for the first $\frac{5}{2}^+$ excited state of Ta^{181} in $(NH_4)_3HfF_7$ in order to solve a controversial question related to the structure of the complex HfF_7 in this compound. The results obtained suggest a structure for HfF_7 and a relaxation mechanism for the angular correlations which are consistent with each other. The relaxation constant λ_2 was found to be $\lambda_2=0.05$ $nsec^{-1}$ at room temperature. A comparison of our results with the different configurations reported in x-ray literature is made.

I. INTRODUCTION

THE angular-correlation experiments reported here were performed in an effort to clarify the details of the structure of the HfF_7^{-3} complex in the compound $(NH_4)_3HfF_7$. This question seemed interesting due to the fact that previous angular-correlation experiments have suggested the existence of time-dependent effects, and because x-ray results on other compounds containing MF_7 radicals have suggested conflicting structures for these radicals.[1]

The experimental evidence most applicable to the structure of $(NH_4)_3HfF_7$ comes from x-ray studies of $(NH_4)_3ZrF_7$ and K_3UF_7, both of which are presumed to be isostructural with the analogous compounds of Hf and Ta. The Zr compound was studied by Hassel and Mark[2] and later by Hampson and Pauling.[3] These latter authors showed that instead of the mixture of HfF_6^{-2} and F^{-3} radicals previously proposed, the compound did indeed contain HfF_7^{-3} radicals. They concluded that group-theoretical considerations would not permit a unique assignment of the positions for the seven fluorine ions in the unit cell, and proposed a structure in which the six fluorines formed an octahedron around the metal ion with the seventh randomly situated in one of the faces.

The major conclusions of Hampson and Pauling were supported by Zacchariesen[4] on the basis of detailed x-ray studies of K_3UF_7. This author, however, concluded that a structure consisting of a pentagonal bipyramid of fluorines surrounding the metal ion was more probable for the UF_7 radical than that proposed by Hampson and Pauling.

Other possible structures that have been suggested for radicals of this type include an arrangement of six of the seven fluorines in a trigonal prism with the seventh ion located above one of the rectangular faces.[1]

Several different groups have studied the compound $(NH_4)_3HfF_7$ by perturbed angular-correlation techniques, using for this purpose the well-known 133–482-keV cascade through the $\frac{5}{2}^+$ state at 482 keV with a lifetime of $\tau_N=15.4$ nsec. Debrunner *et al.*[5] determined the integral angular-correlation coefficients A_2 and A_4 for this compound and noted that the values were unusually high in comparison to other solid compounds studied. Later, Deutsch *et al.*[6] studied the time-differential angular correlation in this material and found a behavior which he suggested was consistent with a pure nuclear-relaxation process. No explanation in terms of the structure of the compound was given. Matthias *et al.*[7] restudied the integral angular correlation in this material as a function of external magnetic field (integral-combined interaction techniques) and found that the results could not be understood in terms of a pure relaxation process. They suggested that the simultaneous presence of a static interaction together with nuclear relaxation might account for the behavior seen. (No theory was available to test this assumption.)

The apparent contradiction between the results of the differential measurements of Ref. 6 and the combined interaction measurements of Ref. 7 led us to reinvestigate this material once again, with the aim of providing a consistent set of experimental results using several different techniques, as well as providing some explanation of the significance of these results in resolving the question of the structure of the HfF_7^{-3} complex raised by the x-ray measurements. As part of an integrated study, simultaneous measurements of the integral and time-differential angular correlations were made on the same source for various values of applied magnetic fields, both at room temperature and at liquid-nitrogen temperature. A self-consistent set of results was obtained, which, when analyzed in terms of the possible structures proposed from x-ray studies, is consistent with a structure consisting of an octahedral arrangement of six fluorines with the seventh moving randomly among the faces.

---

* Work partially supported by Conselho Nacional de Pesquisas, Brasil, Conselho de Pesquisas (UFRGS), and Air Force Office of Scientific Research, Grant No. AF-AFOSR-1280-67.

[1] F. Albert Cotton and Geoffrey Wilkinson, *Advanced Inorganic Chemistry* (Wiley-Interscience, Inc., New York, 1966); Ralph W. G. Wyckoff, *Crystal Structure* (Wiley-Interscience, Inc., New York, 1965), Vol. 3.

[2] O. Hassel and H. Mark, Z. Physik **27**, 89 (1924).

[3] G. G. Hampson and L. Pauling, J. Am. Chem. Soc. **60**, 2702 (1938).

[4] W. H. Zacchariesen, Acta Cryst. **7**, 792 (1954).

[5] P. Debrunner, E. Heer, W. Kündig, and R. Rüetschi, Helv. Phys. Acta **29**, 463 (1956).

[6] M. Deutsch, A. Hrynkiewicz, and R. Stiennig, Massachusetts Institute of Technology Laboratory of Nuclear Science Progress Report, 1959 (unpublished).

[7] E. Matthias, E. Karlsson, A. G. Svensson, K. Johansson, and S. Gustafsson, Arkiv Fysik **30**, 19 (1965).

II. THEORETICAL BACKGROUND

The effect of simultaneous static and time-dependent quadrupole interactions on the angular-correlation function has been discussed in Ref. 8, where the following form for the perturbation factors of the angular correlation was found:

$$G_{K_1K_2}{}^{\mu\mu'}(t)=\sum_{\alpha}\begin{pmatrix} I & I & K_1 \\ \alpha' & -\alpha & \mu \end{pmatrix}\begin{pmatrix} I & I & K_2 \\ \alpha' & -\alpha & \mu' \end{pmatrix} \times e^{-i(\alpha'-\alpha)t}\langle\alpha\alpha'|G^*(t)|\beta\beta'\rangle. \quad (1)$$

The matrix elements $\langle\alpha\alpha'|G^*(t)|\beta\beta'\rangle$ in the above expression appear as combinations of the exponentially decaying eigensolutions of the generalized density matrix given by Redfield[9] in his treatment of nuclear relaxation processes. Several different relaxation processes[10,11] have been described within the framework of this theory including, for example, (a) torsion oscillation: a group of molecules oscillate around an equilibrium position; (b) hindered random molecular rotation in a plane: a molecule or an ion can have several planar orientations in solids, equivalent or not, separated by a potential barrier; and (c) hindered random tridimensional molecular rotation: the molecule or an ion can have an isotropic random motion around a central atom.

One can note qualitatively that the Hamiltonian describing the first two interactions has a nonvanishing time average, which implies the simultaneous presence of static and time-dependent fields acting on the nucleus. The resulting perturbation factor appears as a sum of oscillating terms, each multiplied by a decaying exponential. (In general, the exponential factors multiplying each oscillating term will be different.)

In the third case, the time average of the Hamiltonian describing the fluctuating quadrupole interaction has a vanishing value $\langle H(t)\rangle_t=0$. If at the same time there is no static interaction, the perturbation factor has the simple form

$$G_K(t)=e^{-\lambda_K t}. \quad (2)$$

The effect of a simultaneous magnetic static interaction and a time-dependent electric quadrupole interaction on the angular-correlation function has been determined by Abragam and Pound.[12] For a white spectrum condition $(\omega\tau_c)^2 \ll 1$, the expression for the correlation function becomes

$$W(\theta,t,B)=\sum_{K=0}^{K_{\max}} A_{KK}e^{-\lambda_K t}P_K[\cos(\theta-\omega_B t)]. \quad (3)$$

The time-integrated expression can be seen in Ref. 12.

III. MEASUREMENTS AND RESULTS

In our study of $(NH_4)_3HfF_7$, we measured simultaneously the integral and time-differential anisotropy [defined as $W(180)/W(90)-1$] for the 133–482-keV cascade in the decay of Hf^{181} to Ta^{181}. Studies were made for various values of external magnetic field. A time resolution of 2.5 nsec outside the magnet and 4.5 nsec inside the magnet was obtained for the cascade of interest.

Since the stability of the compound $(NH_4)_3HfF_7$ was unknown, particular care was taken in production of the source. As a check of the technique used to produce the hepta fluoride, nonradioactive samples of both $(NH_4)_3HfF_7$ and $(NH_4)_2HfF_6$ were prepared and studied periodically by x-ray diffraction during three months. The x-ray patterns of both, analyzed following Ref. 13, showed isometric structures with lattice constants of $a=9.5$ Å and $a=8.3$ Å for the hepta- and hexafluorides, respectively, both numbers agreeing with those reported in the literature. No change in composition of the two compounds was seen during the three-month period. As an additional check of the x-ray analysis of our source, we determined the integral angular-correlation coefficients A_2 and A_4, obtaining (-0.11 ± 0.02) and (-0.02 ± 0.02), respectively, in agreement with Ref. 5.

The results of the differential measurements made on $(NH_4)_3HfF_7$ at room temperature are given in Figs. 1–4. In Fig. 1, the behavior of the anisotropy as a function of time without applied magnetic field, is shown. Figures 2–4 give the behavior of the anisotropy with applied magnetic fields of 2.7, 23, and 28.5 kG, respectively. In Figs. 5 and 6, which represent integral measurements, the behavior of the integral anisotropy as a function of the intensity of the applied magnetic field is shown. The result of a differential measurement at liquid-nitrogen temperature is shown in Fig. 7. The experimental results of Fig. 1 agree with those of Ref. 6. The integral results of Figs. 5 and 6 are not in agreement, however, with Ref. 7. We note that the results of Ref. 7 at high magnetic fields could be understood qualitatively if part of the source was actually $(NH_4)_2HfF_6$ instead of $(NH_4)_3HfF_7$.

IV. DISCUSSION AND CONCLUSIONS

The solid lines in Figs. 1–4 represent theoretical results obtained from Eqs. (2) and (3). The values of the relaxation constant have been taken as $\lambda_2=0.04$ nsec^{-1} and $\lambda_2=0.05$ nsec^{-1} in Fig. 1 and $\lambda_2=0.05$ nsec^{-1} in Figs. 2–4. The theoretical curves in Fig. 5 correspond to $\lambda_2=0.04$, 0.05, and 0.068; the result for a very small electrostatic quadrupole interaction is also given. The best agreement between the behavior of our experimental points and theory was obtained with the parameters

---

[8] P. da R. Andrade, J. D. Rogers, and A. Vasquez, Phys. Rev. **188**, 571 (1969); P. da R. Andrade, Ph.D. thesis, Pôrto Alegre, 1968 (unpublished).

[9] A. G. Redfield, IBM J. Res. Develop. **1**, 19 (1957).

[10] Y. Ayant, J. Phys. Radium **17**, 338 (1956).

[11] A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), Chap. X.

[12] A. Abragam and R. V. pound, Phys. Rev. **92**, 943 (1953).

[13] L. Azaroff and M. Buerger, *The Powder Method* (McGraw-Hill Book Co., New York 1958), Chap. 8.

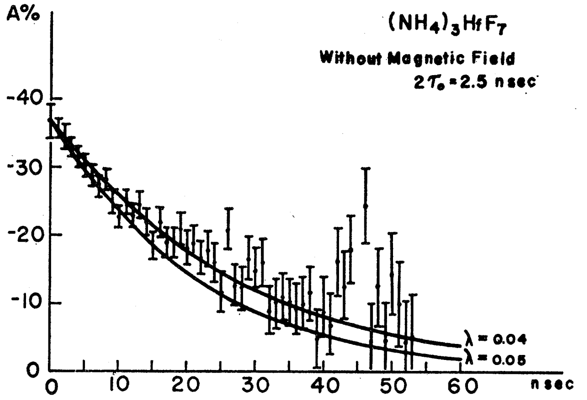

FIG. 1. Experimental anisotropy of the 133–482 γ-γ cascade with $(NH_4)_3HfF_7$ obtained with $2\tau_0=2.5$ nsec. The solid lines are theoretical curves for an isotropic relaxation mechanism with constants $\lambda_2=0.04$ and 0.05 nsec^{-1}.

of Fig. 6. These results show that the attenuation of the angular correlation is consistent with an isotropic fluctuating electric quadrupole interaction, the relaxation constant being very near $\lambda_2=0.05$ nsec^{-1}. To the order of $\omega_0=25\times10^6$ rad sec^{-1} there is no trace of a static interaction.

If we assume that the electronic rearrangement due to the decay of Hf to Ta is equal or faster than 10^{-12} sec, this fluctuating interaction could be caused by a random tridimensional ionic motion occurring in the complex TaF_7^{-3}.

It is of interest to discuss the compatibility of the present results with the different crystalline structures proposed in the literature for $(NH_4)_3TaF_7$.

The pentagonal bipyramid structure seems to be stable and, not having cubic symmetry, should give rise

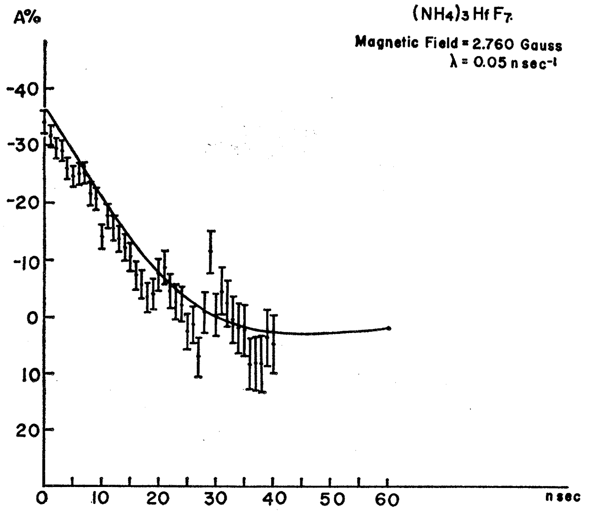

FIG. 2. Experimental anisotropy of the 133–482 γ-γ cascade with $(NH_4)_3HfF_7$ obtained with $2\tau_0=4.5$ nsec. The solid line is the theoretical curve for the behavior of the anisotropy with an applied magnetic field of 2.7 kG and a relaxation constant $\lambda_2=0.05$ nsec^{-1}.

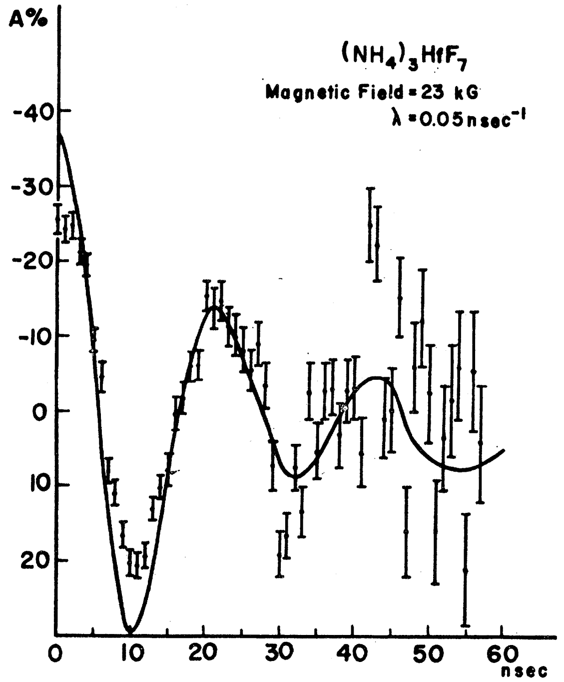

FIG. 3. Experimental anisotropy of the 133–482 γ-γ cascade with $(NH_4)_3HfF_7$ obtained with $2\tau_0=4.5$ nsec. The solid line is the theoretical curve for the behavior of the anisotropy with an applied magnetic field of 23 kG and a relaxation constant $\lambda_2=0.05$ nsec^{-1}.

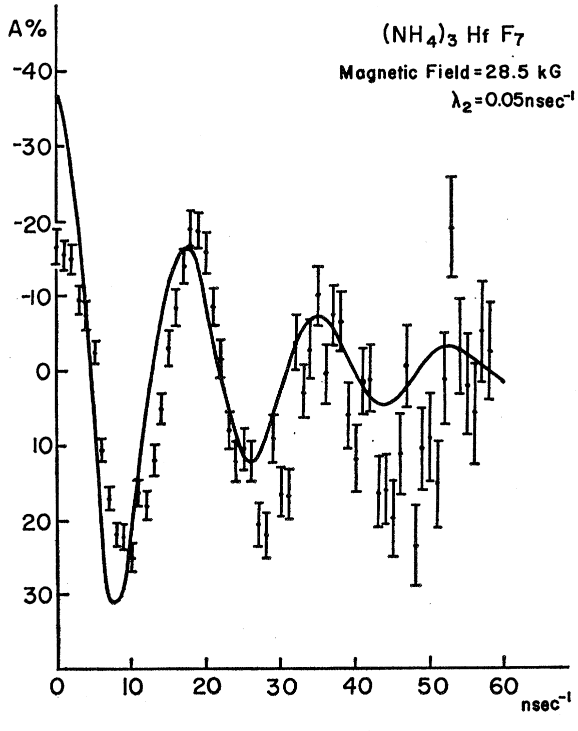

FIG. 4. Experimental anisotropy of the 133–482 γ-γ cascade with $(NH_4)_3HfF_7$ obtained with $2\tau_0=4.5$ nsec. The solid line is the theoretical curve for the behavior of the anisotropy with an applied magnetic field of 28.5 kG and a relaxation constant $\lambda_2=0.05$ nsec^{-1}.

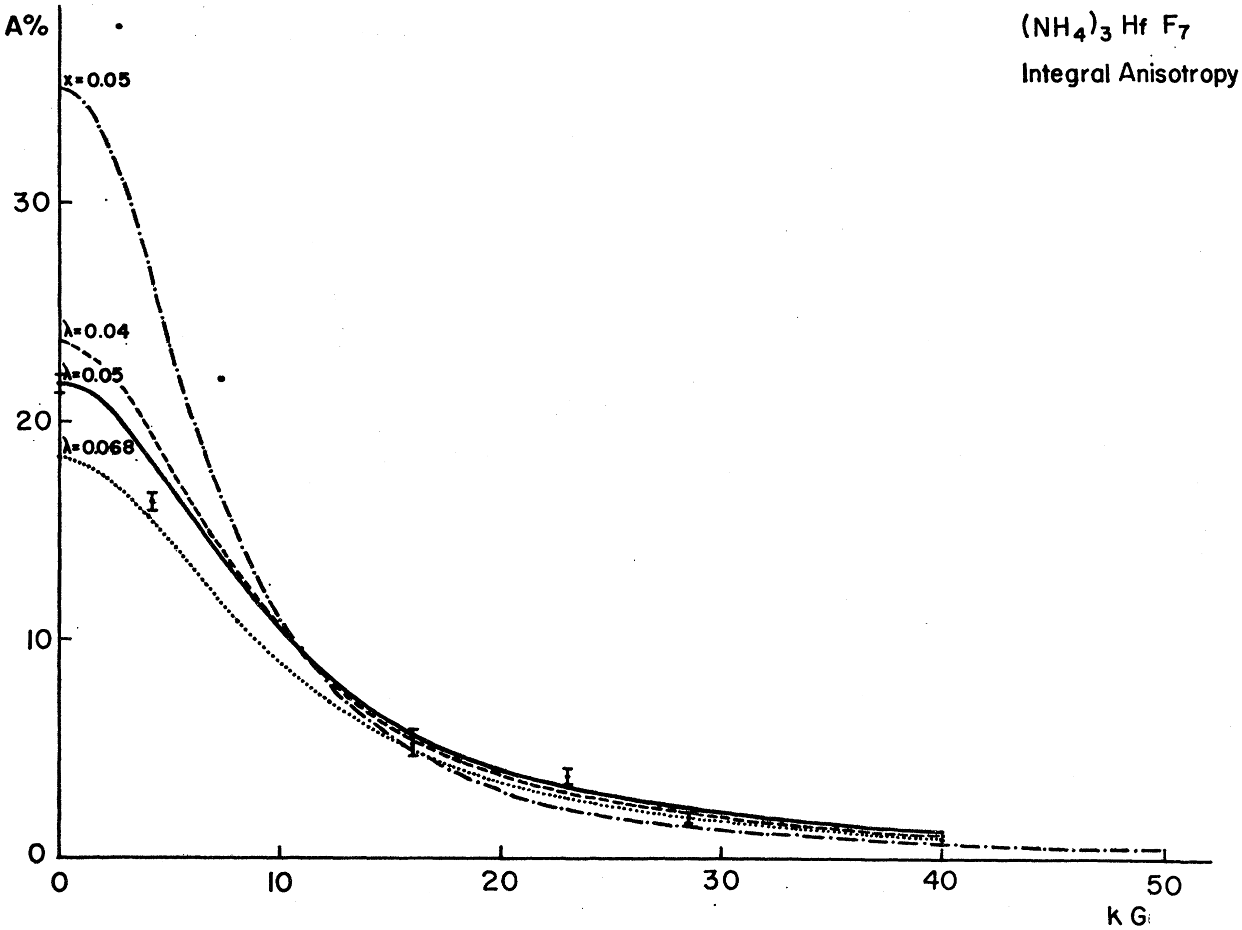

FIG. 5. Comparison of the experimental integral anisotropy (at room temperature) for $(NH_4)_3HfF_7$ as a function of magnetic field with theoretical curves for a small static interaction $\omega_0=25\times10^6$ rad sec^{-1} (where $\chi=\omega_Q\tau_N$) and for several relaxation constants $\lambda_2=0.04$, 0.05, and 0.068 $nsec^{-1}$.

only to a static electric field gradient at the nuclear site. The trigonal prism structure with the seventh ion jumping on its rectangular faces again has no cubic symmetry, and the motion of the seventh ion is a typical ionic rotation in a plane, which would lead to a static contribution plus a relaxation described by more than one exponential. It is to be expected that the field gradient induced by breaking of the cubic symmetry in these cases would be of the order of magnitude of that observed[14,15] in such compounds as HfO_2 or Hf metal, which is at least a factor of 10 greater than the maximum value consistent with the experimental results. Both these structures are, therefore, not compatible with our experimental results.

The octahedron structure with the seventh ion jumping on its faces combines the characteristics of cubic symmetry and isotropic random motion which are in agreement with our results that no static quadrupole interaction is present and that the relaxation can be described by a single exponential. It is interesting to note that the compound $(NH_4)_2HfF_6$ which has the same octahedral structure proposed for the six fluorines in the heptafluoride shows a strong quadrupole interaction,[16] presumably resulting from distortion of the cubic structure. A possible reason for the absence of this strong interaction in the heptafluoride is that the motion of the seventh ion effectively shields the octahedral structure from its surroundings, thus restoring the cubic symmetry.

The experimental result at liquid-nitrogen temperature shows a departure from the behavior at room temperature. In Fig. 7, one may note the appearance of a resonance peak, indicating a possibility that a static interaction is involved, and also the change of the relaxation constant from $\lambda_2=0.05$ $nsec^{-1}$ to $\lambda_2=0.15$ $nsec^{-1}$, clearly demonstrating that the correlation time τ_c has increased by a factor of 3. Two effects might be impor-

---

[14] P. da R. Andrade, A. Maciel, and J. D. Rogers, Phys. Rev. 159, 196 (1967).

[15] P. da R. Andrade, J. Chem. Phys. 50, 5040 (1969).

[16] L. Mayer, E. Bodenstedt, and C. Günther, Z. Physik 177, 28 (1964).

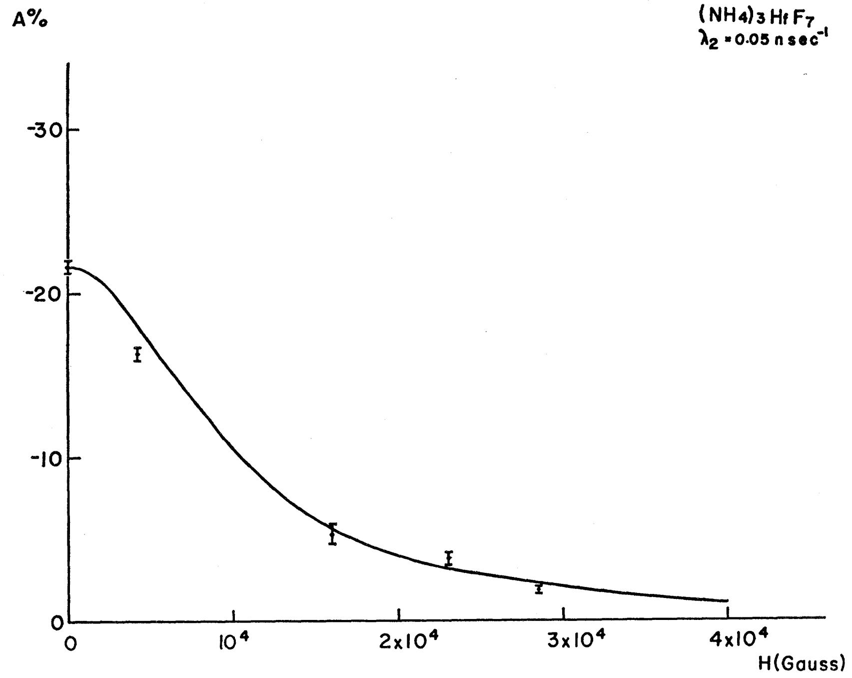

FIG. 6. Comparison of the experimental integral anisotropy as a function of the applied magnetic field for a fluctuating quadrupole interaction with a relaxation constant $\lambda_2=0.05$ nsec^{-1}.

tant: a change of the relaxation mechanism from tridimensional random rotation to torsion oscillation due to the freezing of ionic motions, or the approach of the correlation time τ_c to τ_N leading to a static contribution. This situation is rather complicated for angular-correlation experiments, but it would be worthwhile to have

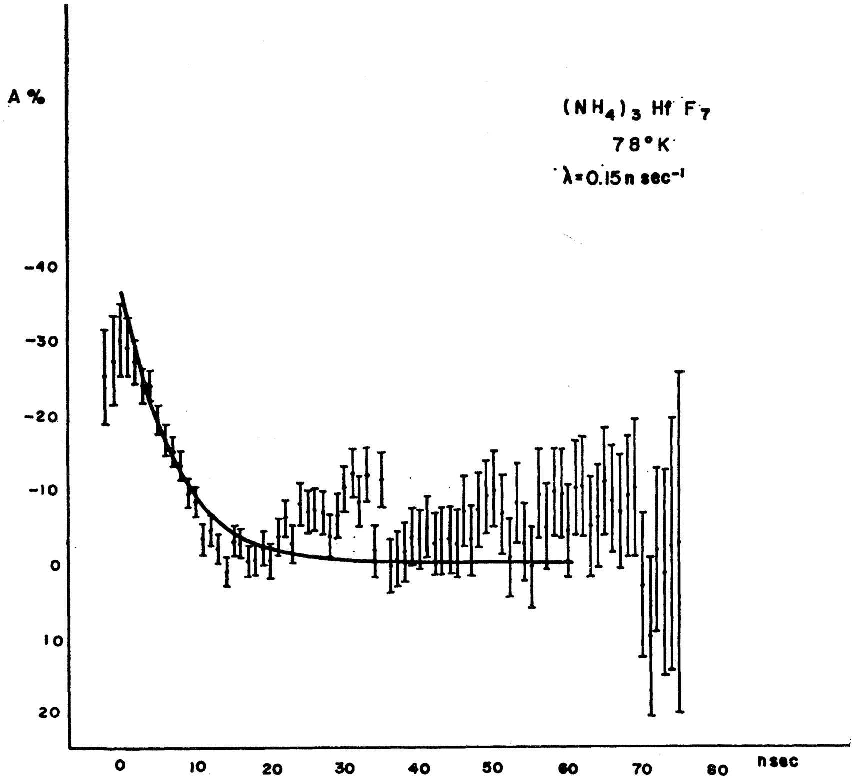

FIG. 7. Experimental anisotropy of the 133–482 γ-γ cascade with $(NH_4)_3HfF_7$ obtained with $2\tau_0=4.5$ nsec at liquid-nitrogen temperature. The solid line is a theoretical curve for a relaxation constant $\lambda_2=0.15$ nsec^{-1}.

experimental curves at different low temperatures by the differential and combined integral techniques to compare to the recent theory developed by Blume and Tjon.[17]

---

[17] M. Blume and J. A. Tjon, Phys. Rev. **165**, 446 (1968).

ACKNOWLEDGMENTS

One of the authors (P. da R. A.) thanks the Conselho Nacional de Pesquisas, Brasil, for a research lecturer fellowship and another (J. D. R.) is indebted to the Pan American Union for support during this work.

PHYSICAL REVIEW B VOLUME 1, NUMBER 7 1 APRIL 1970

Theory and Operation of Proton Spin Refrigerators: Sizable Proton Polarizations[*]

J. R. McColl[†] and C. D. Jeffries
Department of Physics, University of California, Berkeley, California 94720

(Received 25 August 1969)

The enhancement of proton spin polarization by the spin-refrigerator method, in crystals of $Y(C_2H_5SO_4)_3 \cdot 9\,H_2O$ containing a few percent Yb^{3+}, is studied experimentally and theoretically. The spin refrigerator is operated simply by rotating the crystal in a magnetic field at liquid-helium temperatures, or by subjecting the crystal to a pulsed rotating field. The proton polarization comes about because the Yb spins have both anisotropic g value ($g_{\parallel}=3.4$, $g_{\perp}\approx 0$) and relaxation rate ($T_{1e}^{-1}\propto \cos^2\theta \sin^2\theta$), so the Yb spin polarization at $\theta=45°$ can be transferred by cross-relaxation to the protons at $\theta=90°$ by rapid rotation of the crystal or field between these two orientations. A unified theory involving electronic and nuclear spin-lattice relaxation, cross-relaxation, and nuclear spin diffusion explains the results of both types of spin refrigerator, and predicts that polarizations as high as 70% may be achieved at higher operating speeds. Proton polarizations as high as 35% are reported, suggesting application to polarized targets.

I. INTRODUCTION

RECENTLY, Langley and Jeffries[1,2] (LJ) have obtained proton polarizations as high as 19% using a nuclear-spin refrigerator,[3,4] and interpreted their results with a simple, phenomenological model. By extending their measurements and developing a new type of spin refrigerator involving pulsed rotating fields, we have obtained proton polarizations as high as 35% in crystals of $(^{172}Yb,Y)(C_2H_5SO_4)_3\cdot 9H_2O$ (abbreviated as ^{172}Yb:YES). The new results are interpreted in terms of a microscopic theory which predicts that proton polarizations as high as 70% may be achieved under ideal experimental conditions. This polarization is high enough that the spin refrigerator is an interesting possibility for use in polarized proton targets, as an alternative to the dynamic microwave polarization method[5–7] presently being used.

To illustrate a type of pulsed field spin refrigerator, we consider a 1% Yb:YES crystal mounted in the apparatus of Fig. 1. The crystal is oriented with its c axis vertical in a liquid ^4He bath pumped to $\sim 1.2°K$. A copper solenoid which produces a vertical pulsed field $\mathbf{H}_p \sim 15$ kOe of 200-μsec duration is placed in the liquid N_2 (LN) bath for cooling. The apparatus is in the field $\mathbf{H}_{dc}$ of a steel electromagnet capable of producing up to 20 kOe. The YES crystals are diamagnetic except for the Yb^{3+} ions, which behave like spins with $S=\frac{1}{2}$, but with the highly anisotropic g value

$$g^2(\theta)=g_{\parallel}^2\cos^2\theta+g_{\perp}^2\sin^2\theta\,, \qquad (1)$$

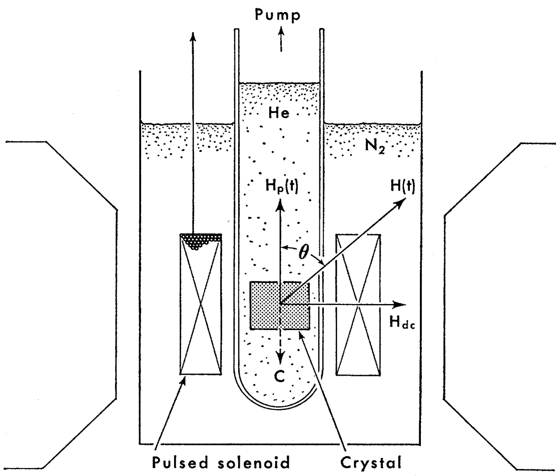

FIG. 1. Experimental arrangement for a pulsed-field spin refrigerator.

---

[*] Supported in part by the U. S. Atomic Energy Commission, Contract No. AT(11-1)-34, Project 20, Report No. UCB-34P20-139.

[†] NSF Predoctoral Fellow. Present address: Physics Department, Yale University, New Haven, Conn. 06520.

[1] K. H. Langley and C. D. Jeffries, Phys. Rev. Letters **13**, 808 (1964).

[2] K. H. Langley, and C. D. Jeffries, Phys. Rev. **152**, 358 (1966).

[3] C. D. Jeffries, Cryogenics **3**, 41 (1963).

[4] A. Abragam, Cryogenics **3**, 42 (1963).

[5] C. D. Jeffries, Phys. Rev. **106**, 164 (1957); **117**, 1056 (1960).

[6] A. Abragam and W. G. Proctor, Compt. Rend. **246**, 2253 (1958).

[7] C. D. Jeffries, *Dynamic Nuclear Orientation* (John Wiley & Sons, Inc., New York, 1963).