Influence of Magnetic Interaction on Nuclear Orientation of Cobalt-60 in Rare-Earth Double Nitrates*

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(Received August 5, 1960)

The effect of ionic spin-spin interactions on nuclear orientation of cobalt-60 in cerous zinc nitrate has been investigated in single-crystal spherical samples cooled below 1°K by adiabatic demagnetization. An experimental demonstration is given that Ce-Co interaction is indeed the cause of the apparently anomalous alignment data. By hypothesizing the existence of a temperature-dependent internal magnetic field, exerted on cobalt ions by cerium dipoles, a simple but quantitatively satisfying description of the observed phenomena is obtained. In the theoretical calculations, measured values of g factors and hfs splittings of cobalt ions in the cerium salt are used. Crystal structure information is invoked only for the purpose of a symmetry argument. The effectiveness of Ce-Zn nitrate as a paramagnetic medium for nuclear orientation experiments is pointed out.

INTRODUCTION

THE popularity of cerous magnesium nitrate,[1] $Ce_2Mg_3(NO_3)_{12}\cdot 24H_2O$, as a paramagnetic medium for nuclear orientation experiments below 1°K depends on its striking thermal and magnetic properties.[2–4] These are (a) its low specific heat, due only to dipole-dipole interaction between cerium ions,[3] which makes possible the attainment of very low temperatures (near 3×10^{-3}°K) by adiabatic demagnetization,[4] and (b) the extreme magnetic anisotropy of the individual cerium ions,[3] a valuable property when small magnetic fields are to be applied.[2]

Unfortunately, in spite of these advantages a general feature of the results is that the anisotropy of gamma-ray emission (a measure of the orientation) is significantly less than that predicted on the basis of the hyperfine structure splittings of the individual ions which contain the radioactive nuclei.[5,6] In addition, the temperature dependence is sometimes quite unexpected, the anisotropy passing through a maximum and decreasing as the temperature is lowered.[5,7] Although it appears reasonable to ascribe such effects to magnetic interactions with the cerium ions which serve as cooling agents, theoretical treatments involving "high"-temperature approximations have failed to account for the discrepancies.[8–10]

In order to study the influence of interactions on the orientation of a nuclide with a well-known decay scheme, we have chosen cobalt-60 incorporated into divalent sites in cerium zinc nitrate (CZN), a crystal isomorphous with CMN but having somewhat more favorable properties for this study, as explained below. The gamma-ray anisotropy has been studied as a function of temperature (or entropy), magnetic field, and concentration of cerium ions. The complete pattern of emission was also checked at the lowest temperature.

We shall show that interaction effects may be quantitatively accounted for by the hypothesis of a temperature-dependent internal magnetic field acting upon the cobalt ions. This field is presumed to be set up by the cerium magnetic moments. Above ten millidegrees interaction effects appear to be negligible.[8]

In the succeeding sections we shall present the relevant properties of CZN, the theory appropriate to this experiment and our modification of it, and a complete comparison with the experimental results.

I. THEORY

A. Resonance Parameters

A calculation of the expected nuclear orientation effects starts with the energy levels and eigenstates of the individual cobaltous ions containing Co^{60} nuclei. These may be deduced from paramagnetic resonance data expressed as values of the parameters in the spin Hamiltonian[11]:

$$\mathcal{H}=g_{\parallel}\beta H_z S_z+g_{\perp}\beta(H_x S_x+H_y S_y)+AI_z S_z+B(I_x S_x+I_y S_y), \quad (1)$$

appropriate to Co^{2+} ions, which have axial symmetry in this salt; the effective spin $S=\frac{1}{2}$. A complication typical

* Supported in part by the National Science Foundation and a contract for helium gas with the Office of Naval Research.

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[1] Abbreviated CMN.

[2] E. Ambler, M. A. Grace, H. Halban, N. Kurti, H. Durand, C. E. Johnson, and H. R. Lemmer, Phil. Mag. 44, 216 (1953).

[3] A. H. Cooke, H. J. Duffus, and W. P. Wolf, Phil. Mag. 44, 623 (1953).

[4] J. M. Daniels and F. N. H. Robinson, Phil. Mag. 44, 630 (1953).

[5] C. M. Schroeder, thesis, Ohio State University, 1957 (unpublished). We are indebted to Dr. Schroeder for sending us graphs of his calculations and experimental results.

[6] E. Ambler, R. P. Hudson, and G. M. Temmer, Phys. Rev. **97**, 1212 (1955); **101**, 196 (1956).

[7] M. A. Grace, C. E. Johnson, N. Kurti, H. R. Lemmer, and F. N. H. Robinson, Phil. Mag. **45**, 1192 (1954).

[8] N. R. Steenberg, Phys. Rev. **93**, 678 (1954).

[9] J. M. Daniels, Can. J. Phys. **35**, 1133 (1957).

[10] W. R. Wright, thesis, Harvard University, 1957 (unpublished).

[11] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A206**, 173 (1951).

TABLE I. Microwave resonance parameters of paramagnetic ions in $Ce_aLa_{2-a}Co_bZn_{3-b}(NO_3)_{12}\cdot 24H_2O$.

Ion	$a=0$, $b=0.005$	$a=2$, $b=0.025$
$Co^{2+}X$:		
$g_\parallel$	4.37±0.01	4.34±0.04
$g_\perp$	4.31±0.01	4.28±0.04
$A(Co^{59})\times 10^4$ cm^{-1}	98.9±0.5	95±2
$B(Co^{59})\times 10^4$ cm^{-1}	94.5±0.5	95±2
$A(Co^{60})\times 10^4$ cm^{-1}	56.2	54.3
$B(Co^{60})\times 10^4$ cm^{-1}	54.3	54.3
$Co^{2+}Y$:		
$g_\parallel$	7.362±0.010	7.18±0.10
$g_\perp$	2.337±0.005	2.38±0.08
$A(Co^{59})\times 10^4$ cm^{-1}	292±1	291±15
$B(Co^{59})\times 10^4$ cm^{-1}	<3	<30
$A(Co^{60})\times 10^4$ cm^{-1}	167.5	166
$B(Co^{60})\times 10^4$ cm^{-1}	<2	<20
Ce^{3+}:		
$g_\parallel$	···	0.25±0.05
$g_\perp$	···	1.823±0.007

of the double nitrates occurs in CZN, namely that Co^{2+} ions (or rather hydrated complexes $[Co\cdot 6H_2O]^{2+}$) occupy two different types of crystallographic sites called "X sites" and "Y sites."[12] These sites give different distortions to the cobaltous ions and consequently different magnetic properties[11] which may be characterized as nearly isotropic and highly anisotropic, respectively.[12] Table I lists the g factors and hfs constants in Eq. (1) for small amounts of cobalt in CZN and isomorphous diamagnetic lanthanum zinc nitrate (LZN), and for cerium. Though broadened by the presence of cerium, the cobalt spectra in CZN were sufficiently resolved to determine the parameters to the precision specified. As Table I indicates, A and B are measured for Co^{59} and have to be scaled for Co^{60} using the known spin and magnetic moment of each.[13]

In samples of LZN containing no Ce and 0.5% Co, the relative numbers of X and Y ions were calculated from the ratio of intensities of the two spectra, corrected for the relative sizes of the matrix elements for the transitions observed. The result obtained was $N_X/N_Y=1.80\pm0.20$. This ratio is more difficult to measure in crystals containing large amounts of cerium, for the reasons discussed in another paper.[14] Thus it was not possible to determine directly the ratio for one of the samples actually used in these experiments. Nor were the resonance measurements sufficiently extensive or precise to show whether the ratio varies with cobalt or cerium concentration, conditions of crystal growth, etc. For these reasons we have allowed a restricted variation in the ratio to give a best fit of the orientation data.

A comparison of Table I with resonance data for CMN[12,15] shows a high degree of similarity, including the value of N_X/N_Y. This latter fact was somewhat disconcerting in that our original motivation for choosing the Zn salts, rather than Mg, was the hope of significantly influencing the N_X/N_Y ratio by virtue of the near equality in size of cobalt and zinc ions. However, when our initial orientation experiments showed that CZN produces substantially larger gamma anisotropies than does CMN,[5] we elected to continue work on the Zn salts because of their potentially greater usefulness. In addition, the fact that the anisotropy again passed through a maximum indicated that strong Ce-Co interaction might be present in CZN and could be conveniently studied in this salt.

B. Energy Levels and Populations

Eigenvalues E_i of the energy matrix corresponding to Eq. (1) are easily obtained, since in all cases of present interest the matrix breaks up into 2×2 submatrices. Thus the eigenstates ψ_i are linear combinations of two eigenstates ψ_m of I_z with mixing coefficients C_{im}; m is the nuclear magnetic quantum number giving the projection of the nuclear spin on the symmetry axis (z axis). Assuming the cobalt ions are in equilibrium at temperature T, a normalized Boltzmann population distribution (N_i/N) over the energy levels of Co^{60} may be computed, where we have let N_i=number in state ψ_i and N=total number of nuclei.

C. Angular Distribution

Steenberg[16] has shown that the angular distribution of either gamma ray emitted in the Co^{60} decay scheme $[5(\beta,1)4(\gamma,2)2(\gamma,2)0]$ is

$$W(\theta)=\sum_{m=-5}^{+5}(N_m/N)W_m(\theta), \tag{2}$$

where the relative population of state ψ_m is given by

$$(N_m/N)=\textstyle\sum_i C_{im}^2(N_i/N), \tag{3}$$

and the angular distribution of radiation from this state is

$$W_m(\theta)=1-(1/21)(m^2-10)J_2P_2(\cos\theta) -(1/252)(m^4-25m^2+72)J_4P_4(\cos\theta). \tag{4}$$

Here θ is the polar angle measured from the axis of orientation; P_2 and P_4 are Legendre polynomials. J_2 and J_4 are attenuation factors due to finite counter geometry, and were 0.9325 and 0.803, respectively, for our counters.[17] The effect of the preceding β transition is included in Eq. (4), and it is assumed that no reorientation effects occur in the intermediate states of the cascade.

After calculating $W(\theta)$ for the X and Y ions individually, we computed a weighted superposition:

$$W(\theta)=(1/N)[N_XW_X(\theta)+N_YW_Y(\theta)] \tag{5a}$$

$$=1+A_2P_2(\cos\theta)+A_4P_4(\cos\theta). \tag{5b}$$

[12] R. S. Trenam, Proc. Phys. Soc. (London) **A66**, 118 (1953).
[13] J. E. Mack, Revs. Modern Phys. **22**, 64 (1950); also W. Dobrowolski, R. V. Jones, and C. D. Jeffries, Phys. Rev. **101**, 1001 (1956).
[14] J. W. Culvahouse, W. Unruh, and R. C. Sapp (to be published).
[15] W. B. Gager, P. S. Jastram, and J. G. Daunt, Phys. Rev. **111**, 803 (1958).
[16] N. R. Steenberg, Proc. Phys. Soc. (London) **A65**, 791 (1952).
[17] See A. L. Stanford, Jr., and W. K. Rivers, Jr., Rev. Sci. Instr. **30**, 719 (1959).

Finally, letting $\theta=0$ and $\pi/2$, one obtains the anisotropy ϵ as it is customarily defined[16]:

$$\epsilon=1-W(0)/W(\pi/2). \quad (6)$$

Such calculations were carried out as functions of $(1/T)$ for externally applied fields of zero and 300 oersteds, completely neglecting interactions and using the parameters appropriate to diamagnetic LZN. In Sec. III the results will be displayed along with the experimental data for direct comparison. Further presentation of theory, modified to include Ce-Co interactions by an internal-field model, will be postponed to Sec. IV, after the relevant experiments have been discussed in Secs. II and III.

II. EXPERIMENTAL DETAILS

Since our experimental procedures are quite standard in the nuclear orientation field,[18] we shall mention them briefly and concentrate our attention on those aspects which are most germane to the discussion of results.

A. Samples

About 60 μC of Co^{60} activity was incorporated in each of two spherical single crystals[19] of CZN weighing 1.7 g.[20] In one crystal, the activity was homogeneously distributed throughout the sphere; we shall call this the "homogeneous" sample. Actually, this sample was not exactly spherical, the surface having a flat spot and a small surface fissure resulting from handling. Also, the interior was cloudy so that it was difficult to distinguish the orientation of the crystal axis with any precision. In spite of these imperfections, we believe that the results fairly represent the behavior of Co^{60} in a clear, spherical crystal of CZN, more so than, for example, would an elongated or flat sample with shape corrections of dubious validity applied. Microwave resonance of this sample gave g factors and hfs splittings consistent with Table I.

To test for the presence of interaction effects by reducing the concentration of cerium, we decided to effect a complete separation of the cobalt from the cerium.[21] This was accomplished by confining the Co^{60} to a thin layer (about 0.1 mm thick) of LZN grown into the equatorial plane of a CZN sphere. Growth of the sphere was necessarily in three stages: first the lower hemisphere was grown, then the layer was deposited on it,[22] and finally the upper hemisphere was grown. The resulting specimen contained 60 μC of activity; it was clear inside so that the crystal axis could be easily distinguished when the sample was oriented for mounting. In this sample, termed the "layered" sample, Ce-Co magnetic interaction should be completely negligible. Of course, adequate thermal contact between the cobalt-doped layer and the bulk of the cerium ions is required to insure cooling of the layer to the temperature of the cerium spin system. (This requirement appears to be satisfied only at the lowest temperatures, from the data presented in Sec. III. We leave further discussion of the heat transport problem for that section.)

B. Cryogenics

The specimen was suspended by taut threads from a glass frame imbedded at either end in CrK alum guard salts in such a way that the crystal axis was horizontal and mutually perpendicular to the (horizontal) field of a large iron electromagnet and to the (vertical) axis of a pair of mutual inductance bridge coils. The entire assembly was placed inside the sample chamber in a demagnetization cryostat which could be translated from the electromagnet into an arrangement of two counters and a pair of electronically regulated pseudo-Helmholtz coils which could be rotated about a vertical axis. Warmup times of several hundred seconds occurred, leading us to estimate an average heat leak of about 2–3 erg/sec, of which 1 erg/sec was radioactive heating. This estimate is based on the expectation, confirmed by experiment,[23] that the thermal capacity of CZN is about that of CMN.[3,4]

A transistorized version[24] of the electronic mutual inductance bridge designed by Pillinger, Jastram, and Daunt[25] was employed to monitor the susceptibility χ' of the sample at a frequency of 148 cps. The amplitude of the measuring field was about 0.05 oersted rms. Calibration in the 1–4°K temperature range yields the magnetic temperature parameter T^*; the T^*-T relationship for CZN is unknown, although it is probably similar to that of CMN.[4,26] Because of this uncertainty, we have plotted all experimental results as functions of $1/T^*$, and shall simply ignore any differences between T^* and T when comparing with theory. We feel the difference is probably not of crucial importance for our discussion here. It should be noted that T^* in our work refers to a round sample, for which the departure from T should be less than for other shapes in the paramagnetic region. On the other hand, the T^*-T

[18] See the review article by R. J. Blin-Stoyle and M. A. Grace, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 42, p. 555 ff.

[19] Round single crystals were produced by the method of C. M. Schroeder, Rev. Sci. Instr. **28**, 205 (1957).

[20] The amount of cobalt present in our samples when finally prepared is believed to be about 0.005 atomic percent, of which most is of course Co^{59}.

[21] Other dilution experiments have been reported by N. Kurti [Phys. Today **11**, 19 (1958)] who used a 10% concentration of cobalt ions for cooling Co^{60} in LMN; only small anisotropies were produced. C. M. Schroeder (reference 5) tried 50% replacement of cerium by lanthanum.

[22] Independent tests had shown that redissolving of the crystal can be avoided if properly saturated solutions are used.

[23] A plot of entropy S/R versus the square of reciprocal magnetic temperature T^* in the high-temperature region (see reference 4) yields for CZN the specific heat constant $(6.2\pm0.2)\times10^{-6}R$.

[24] Full details are given in M. W. Levi, PhD. thesis, University of Kansas, 1960 (unpublished).

[25] W. L. Pillinger, P. S. Jastram, and J. G. Daunt, Rev. Sci. Instr. **29**, 159 (1958).

[26] D. de Klerk has criticized the T^*-T relationship for CMN given by Daniels and Robinson in reference 4; see *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 15, p. 118.

relationship will depend on the type of ordering at the lowest temperatures. Also, in the ordered region T^* measured at 148 cps may differ appreciably from T^* measured at lower frequencies, ballistically, or statically.[27]

A large number of adiabatic demagnetizations from fields between 3 and 25.5 kg and bath temperatures from 0.95 to 1.15°K have been carried out, and only data extrapolated back in time to the instant of demagnetization have been used. These procedures eliminate distortion of the data due to inhomogeneous heat transfer. The exact time of demagnetization was known to within about two seconds, causing an uncertainty in extrapolation of ± 2 in $1/T^*$ but usually a negligible error in the counting rates; see Sec. II D.

C. Counters

Gamma radiation detection was accomplished with two scintillation counters employing 1×1-inch NaI(Tl) crystals, 6199 phototubes, and their associated linear amplifiers and pulse-height selectors. Electronic scaling strips with a capacity of 100 000 counts per channel fed a printer, the read-out-and-reset operations being automatically triggered by a synchronous timer every 25 seconds.

Tests for counter drifts were carried out by occasional "dummy runs"; the equipment had adequate short-term stability of 1–2%, necessitating no important drift corrections. Interchange of counter position served as a further check.

For work in external magnetic fields up to 300 oersteds, Conetic[28] shields provided quite satisfactory magnetic shielding for the phototubes, which were also fitted with Lucite light pipes. Though the resolution is poor with the light pipes, this is not important when working with Co^{60}. Only the photopeaks of the pulse spectrum were accepted by the pulse-height analyzers, effectively discriminating against background and scattered gammas.

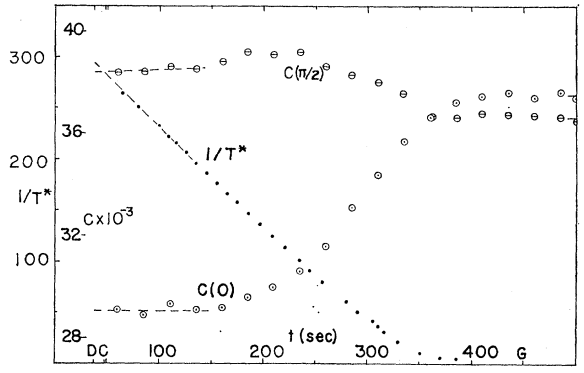

FIG. 1. Warmup curves showing inverse magnetic temperature and counting rates parallel and perpendicular to the crystal axis vs time for Co^{60} in the homogeneous specimen of Ce-Zn nitrate ($H_{ext}=0$) following adiabatic demagnetization at an entropy of $0.28R$. The letters D, C, and G denote the times when the demagnetization was completed, when the counting cycle commences, and when exchange gas was admitted to the sample chamber, respectively.

[27] C. W. Dempesy and R. C. Sapp, Phys. Rev. **110**, 332 (1958).
[28] Trademark, Perfection Mica Company.

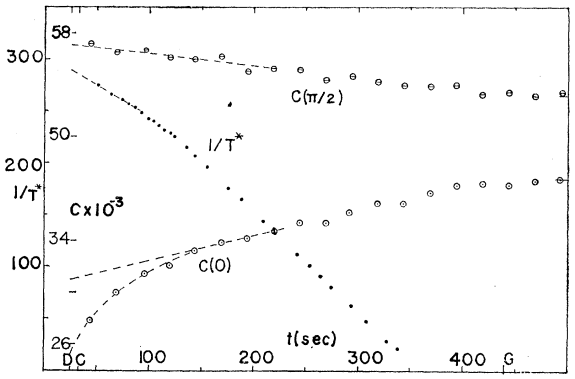

FIG. 2. Warmup curves showing inverse magnetic temperature and counting rates parallel and perpendicular to the crystal axis vs time for Co^{60} in the layered specimen of Ce-Zn nitrate under the same conditions as those listed with Fig. 1; the letters D, C, and G have the same significance.

The front faces of the counters were 35 mm from the center of the source, leading to the counter geometry correction factors previously quoted in Sec. I C. No source extension or decentering corrections were applied; these are corrected in first order by the normalization described in the next section.

D. Data Analysis

Counter and bridge readings were plotted as functions of time for each demagnetization, and extrapolated back to the time of demagnetization to obtain $1/T_0^*$ and the counter readings $C_0(\theta)$ under conditions of homogeneous equilibrium. Dividing $C_0(\theta)$ by the counting rate at the end of a warmup, $C_\infty(\theta)$, gives a normalized counting rate directly proportional to $W(\theta)$.

Most of the extrapolations were straight lines, unless the data points definitely indicated a curvature. Limits of reasonable variation in $1/T_0^*$ and $C_0(\theta)$ were estimated by eye; in $1/T_0^*$ these were negligible and in $C_0(\theta)$ they were usually no greater than the statistical spread calculated from the recorded number of counts per 25 second interval ($30\times10^3-50\times10^3$ counts).

The validity of the extrapolation procedure is illustrated by Figs. 1 and 2 which show typical plots of the raw readings for the homogeneous and the layered samples, respectively. We dwell on this point because it illustrates a common problem ininterpreting adiabatic demagnetization data. Though it is necessary to extrapolate to get meaningful values of the parameters being observed, at the same time some uncertainty is introduced. Inspection of Figs. 1 and 2 show that little difficulty is encountered in dealing with $1/T^*$, or with the counting rates for the homogeneous sample. On the other hand, $C(0)$ for the layered sample is harder to handle, since the extrapolation is curved and must

be extended over nearly 20 seconds. It is quite possible to make an incorrect estimate of $C_0(0)$ in such cases as Fig. 2 depicts, especially in the direction of overestimating the gamma anisotropy by several percent.

We should like to suggest a qualitative reason for the time dependences seen in Fig. 2. The transient behavior of both $C(\theta)$ and $1/T^*$ seems consistent with rapid initial cooling of the layer by at least a portion of the CZN in good thermal contact with it, within the time required to get the first readings. Further, we note that a change in $d(1/T^*)/dt$ occurs at about 130 sec, at which time $dC(0)/dt$ also reaches a steady value; this may indicate that a temperature difference large enough to conduct beta-ray heat out of the layer has evolved during this time.

E. Misalignment Error

Aside from the extrapolation problem, it is also necessary to estimate the possible error due to misorientation of the counters relative to the crystal axis. This is particularly important along the axis, where the greatest change of counting rate is ordinarily observed with Co^{60}. Experimentally, we could rotate our counter circle in the horizontal plane until the maximum anisotropy was reached; this procedure, however, did not enable us to establish whether the crystal axis was exactly in the horizontal plane. We believe that the counter misalignment did not exceed 5°, for which the effect on the anisotropy [Eq. (6)] does not exceed 1.5%.

III. RESULTS

In the following sections we shall present and discuss the results for the two samples investigated. The case of zero external field (nuclear alignment), being most sensitive to interactions, will be dealt with first. Some of the results for an external field (nuclear polarization) may also require internal field effects for interpretation, although the comparison is less sure because of influence of the field on the magnetic thermometer.

A. Homogeneous Sample in Zero External Field

In Fig. 3 the open circles show the dependence of the experimentally determined ϵ on $1/T^*$, together with a theoretical curve of ϵ vs $1/T$ neglecting interactions, calculated as described in Part I. For this curve we took the ratio $N_X/N_Y=1.6$ since this value gives a somewhat better fit at "high" temperatures ($1/T<100$) than does 1.8, the value obtained from microwave resonance on LZN. Note that this variation is not outside the limits of uncertainty in the microwave value, since as previously remarked, it was not possible to estimate N_X/N_Y precisely for CZN from the resonance intensities. The sensitivity of ϵ to this change in N_X/N_Y at $1/T=100$ is only about 1.5%.

We want to emphasize that the theoretical curves in Fig. 3 are based on single-ion resonance parameters

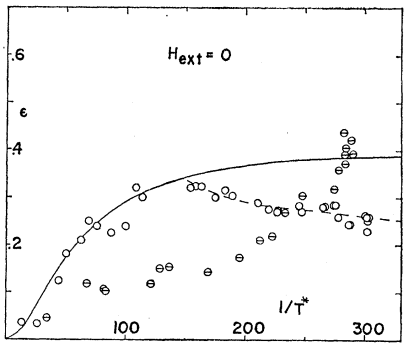

FIG. 3. Anisotropy of gamma radiation due to alignment of Co^{60} in round single crystals of Ce-Zn nitrate in zero external field. The theoretical curve for ϵ is calculated, neglecting interactions, as a function of $1/T$ using the resonance parameters in Table I for this salt and taking $N_X/N_Y=1.6$. The upper curve neglects interactions while the dashed curve includes Ce-Co interaction by the internal field model described in Sec. IV of the text. The experimental points, vs $1/T^*$, are plotted for the homogeneous sample as open circles, the size of which indicates the estimated uncertainty. The circles with lines through them represent data for the layered sample under similar conditions.

measured in CZN (with a small sacrifice in precision) and therefore cannot reasonably be doubted as to their relevance.[8] Having chosen N_X/N_Y as explained in the preceding paragraph, the only other important uncertainty is the T^*-T relation, which should not affect the high-temperature fit. Since no physically reasonable T^*-T relation could distort the $\epsilon(1/T)$ curve in this manner, the phenomenon is attributed to Ce-Co spin-spin interaction.[15]

B. Layered Sample in Zero External Field

Study of the layered sample represents an attempt to demonstrate *experimentally* that the temperature dependence of ϵ is indeed caused by Ce-Co interaction. Such a demonstration seems desirable since, as Daniels has emphasized,[9] the mere fact the cerium broadens the cobalt resonance lines[14,15] is incomplete evidence for perturbation of the nuclear orientation by this mechanism. Keeping in mind the possibility of insufficient cooling, we see in Fig. 3 anisotropies for the layered sample which are in direct contrast with those for the homogeneous sample. In particular, note that at the lowest temperatures ϵ equals (and even appears to exceed) the expected value. Part of this steep rise is undoubtedly due to the fact that $1/T^*$ becomes relatively constant while $1/T$ is really considerably larger. Also, there is some danger of overestimating by several percent the value of ϵ, for the reason explained in Sec. II D.

At higher temperatures we feel that the small values of ϵ reflect inadequate cooling of the Co^{60}-doped layer because the portion of the CZN in good thermal contact with the layer has too little heat capacity to cool the layer close to the temperature of the bulk of CZN. (In this connection it seems significant to us that the steepest rise of ϵ occurs precisely in the temperature

range where the cerium specific heat is expected to become large.[23]) Since ϵ and $1/T^*$ represent average properties of different parts of the sample, anisotropies of about 10% can be explained assuming that the layer comes to equilibrium with only a thin slice of CZN roughly 0.1 mm thick. Presumably this would be the distance through which heat is transported in a few seconds after demagnetization. Thereafter, heating by beta absorption would cause the temperature of the layer of rise. As these estimates are rather crude, and present information on heat transport in paramagnetic salts at very low temperatures is quite meager,[29] we can only claim to have suggested a reasonable qualitative explanation for the temperature dependence of the layered-sample data. Nevertheless, the relative values of ϵ for the two samples at the lowest temperatures clearly indicate the extent of Ce-Co interaction effects, which was our primary objective. We have rejected as unlikely the hypothesis that thermal equilibrium between Ce and Co ions is achieved at the lowest temperature more rapidly in the layered sample than in the homogeneous sample, a possibility which could be invoked to account for the differences noted in Fig. 3.

C. Radiation Pattern at Low Temperatures

In order to see whether the anomalous temperature dependence of ϵ for the homogeneous sample might reflect the evolution of an unusual radiation pattern, we undertook some studies of the pattern itself. Such a procedure is particularly advisable when nuclear orientation effects depart from simple expectations.[30] The

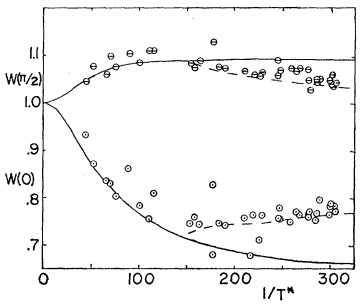

FIG. 4. Angular distribution of Co^{60} gamma rays in directions perpendicular (upper part) and parallel (lower part) to the crystal axis of Ce-Zn nitrate in zero external field as functions of $1/T^*$. Theoretical dependence of $W(0)$ and $W(\pi/2)$ on $1/T$ is also graphed for $N_X/N_Y=1.6$ with interactions neglected (solid curves), and included (dashed curves) by the internal field model described in Sec. IV of the text.

[29] Assuming that heat transfer is a diffusion process in paramagnetic salts at very low temperatures, as is suggested by C. G. B. Garrett, *Magnetic Cooling* (Harvard University Press, Cambridge, Massachusetts, 1954), p. 90, a consequence of the very poor diffusivity of such media is that heat is propagated very inhomogeneously, essentially as a "thermal shock wave."

[30] In simple situations ϵ is a convenient single parameter which completely characterizes the nuclear orientation; from the experimentalist's viewpoint its dependence on the ratio $W(0)/W(\pi/2)$ has the advantage of minimizing the effect of certain counting errors such as that due to random timing scatter.

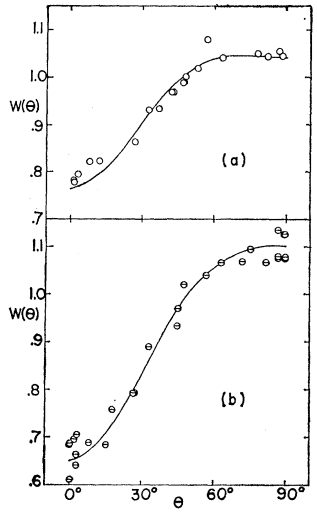

FIG. 5. Angular distributions $W(\theta)$ of Co^{60} gamma radiation from Ce-Zn nitrate at an entropy of $0.28R$; $H_{ext}=0$. (a) Homogeneous sample results compared with theory including interactions (Sec. IV of text), $1/T=300$. (b) Layered sample results fitted to theory neglecting interactions at $1/T=300$. Solid curve is $1-0.267P_2-0.083P_4$.

reason for this is that the definition of ϵ [Eq. (6)] involves only the *ratio* $W(0)/W(\pi/2)$, and therefore in principle it conveys less information than do $W(0)$ and $W(\pi/2)$. In addition, if multiaxial spin alignments are developed, due for example to domains of spatially ordered spins, the values of $W(0)$ and $W(\pi/2)$ themselves might not adequately characterize the complete radiation pattern $W(\theta,\phi)$, where θ, ϕ are spherical polar angles relative to the trigonal axis (z axis) and a hexagonal axis (x axis) of the crystal.[14]

Hence in Fig. 4 are displayed $W(0)$ and $W(\pi/2)$ as functions of $1/T^*$ for the homogeneous sample. Further, we show the pattern $W(\theta)$, with $0\leq\theta\leq\pi/2$, at the lowest temperature in Fig. 5(a). (No ϕ dependence in the $\theta=\pi/2$ plane was found.) For comparison we have included Fig. 5(b), which shows the full pattern $W(\theta)$ for the layered sample, under the same conditions as in Fig. 5(a).

In Sec. IV we shall offer an internal-field model for magnetic interactions which provides a reasonable explanation of the data, as may be seen from the curves in Figs. 3, 4, 5(a) computed from that model.

D. Orientation in Applied Magnetic Fields

In order to determine the magnitude of gamma anisotropy produced by moderate applied magnetic fields, and to explore the possibility of interaction effects in this case, we undertook such experiments and shall next report the results for the case of 300 oersteds applied parallel to the crystal axis.

In this investigation we encountered a typical experimental complication, namely, that the presence of the field had a strong temperature-dependent influence on the operation of the ac bridge. This field influence was particularly bad for the homogeneous sample, preventing us from getting a precise calibration. Because of this difficulty we had to adopt the following procedure: the bridge readings were converted to $1/T^*$ using cali-

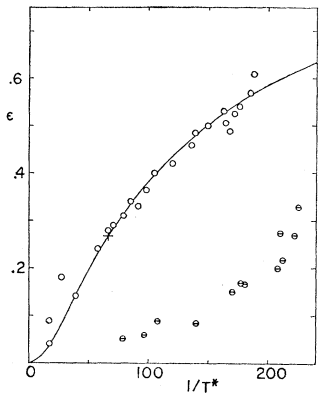

FIG. 6. Anisotropy of Co^{60} gamma rays from Ce-Zn nitrate samples in $H_{ext}=300$ oe as functions of $1/T^*$. Upper data points are for the homogeneous sample, the lower for the layered sample. A theoretical curve $\epsilon(1/T)$ neglecting interactions is also shown, having been adjusted to fit the experimental data at $1/T^*=66$.

bration constants chosen to make the observed and calculated anisotropies coincide at $1/T^*=66$, where we expect that misalignment and magnetic interaction effects should have negligible influence. The calibration constants thus required were not outside the rather broad range of possible values determined at helium temperatures.

Results of this experiment are displayed in Fig. 6, which shows for the homogeneous sample a quite good fit, over the entire temperature range, to a theoretical curve computed without the inclusion of any internal fields at all. Though it is tempting to interpret this fit as meaning that our 300-oersted field was sufficient to erase magnetic interaction effects completely, we think it dangerous to rule out entirely the possibility of a fortuitous combination of external and internal fields, superimposed on a temperature change, for $1/T^*$ greater than about 100, say. It is reasonable to expect some influence by an applied field whenever the g factor in the direction of the field is nonzero. Thus temperature shifts, susceptibility changes, and possible relaxation effects may all be present, rendering it extremely difficult to assess the validity of the apparently simple interpretation of Fig. 6.

For completeness we have included comparable data for the layered sample in Fig. 6. Apparently the application of the field increased the heat capacity of the Co-doped layer without sufficiently improving the heat capacity of the adjacent CZN. Thus one might again attribute low values of ϵ to insufficient cooling of the Co^{60}, for the reasons given in III B.

It is perhaps appropriate to point out here that we have not established the existence of large degrees of nuclear "polarization," as opposed to "alignment," since ϵ is sensitive only to the latter.[18] One is justified in deducing the former from ϵ only if the orientation mechanism and its perturbations are fully understood. Our reasons for emphasizing caution in this matter, in spite of the apparently good agreement seen in Fig. 6, may be appreciated by referring to the degree of circular polarization of gamma rays from Co^{60} in CMN.[31]

[31] J. C. Wheatley, W. J. Huiskamp, A. N. Diddens, M. J. Steenland, and H. A. Tolhoek, Physica **21**, 841 (1955).

This quantity, which directly reflects nuclear polarization, reaches a surprisingly low saturation value as the temperature is lowered, in spite of large and continuously increasing anisotropy. Therefore, it may be important to re-examine the interpretation of the parity experiments[32] in the light of possible perturbation by magnetic interactions. It would also be desirable to determine the degree of nuclear polarization of Co^{60} in CZN by means of a circular polarization experiment, in order to establish the actual degree of nuclear polarization.

IV. DISCUSSION

In the previous section we presented data which demonstrates the existence of perturbation of nuclear orientation by magnetic interaction, and shows quantitatively the magnitude of its effect on the gamma radiation pattern of Co^{60} in CZN. Now we shall discuss a theoretical model in which interactions are treated as an equivalent internal magnetic field; the results of Fig. 3 will be interpreted on the basis of the model. This extension of the theory of Sec. I is necessitated by the insufficiently fast convergence of treatments based on expansions in powers of $1/T$.[8–10]

A. Internal Magnetic Field Model for Magnetic Interaction

The internal-field model is founded on the known magnetic properties of cerous ions and their interaction with cobaltous ions in this crystal, using some recent paramagnetic resonance[14] and x-ray powder diffraction work.[33] (A more extended discussion of the x-ray data and a model for the CZN unit cell appears in reference 14.)

It suffices for the argument below to summarize the situation as follows: the cerium ions, in the equivalent hexagonal description of the rhombohedral lattice, lie in layers perpendicular to the trigonal axis; when occupying the general position at the center of the unit cell (Y site), a cobalt ion is halfway between planes of cerium ions; in the two special positions (X sites) cobalt ions are nearly in a cerium layer on an axis through the center of a triangle of cerium ions.

Now the direction of the dipolar field cast by cerium ions at the cobalt sites[14] should be chiefly perpendicular to the crystal z axis. This follows from the cobalt positions mentioned in the preceding paragraph and the fact that for Ce^{3+} $g_\perp \gg g_\parallel$ (Table I), so that effectively the ceriums are dipoles constrained to lie in the xy plane.

Next, we suppose that at low temperatures, groups of cerium spins are statically ordered parallel to certain local axes in the xy plane, with the directions of these ordering axes showing the over-all trigonal symmetry

[32] C. S. Wu, E. Ambler, R. W. Hayward, D. D. Hoppes, and R. P. Hudson, Phys. Rev. **105**, 1413 (1957); **106**, 1361 (1957).

[33] J. W. Culvahouse and R. C. Sapp (unpublished).

of the whole crystal. Thus a random distribution of cobalt ions would experience dipolar fields in one of three possible directions in the xy plane, 120° apart, with equal probability. At present we are unprepared to go into such questions as the amount of long- or short-range order, whether the ordering is ferromagnetic or antiferromagnetic, what kind of domains might be present, what directions the cerium dipoles point in the xy plane, etc. In any case, our comparison with the results in Sec. III appears to be not particularly sensitive to such details.

Taking the externally applied field to be zero, the calculation proceeds by obtaining $W_X(\theta^*,H_{\rm int})$ for three equal groups of X ions (with $A=B$), where θ^* is the polar angle referred to the direction of $H_{\rm int}$ acting on that group. Y ions ($A\gg B$) are quite insensitive to small fields up to a few hundred oersteds in the perpendicular direction, so that $W_Y(\theta)$ is essentially unchanged. The over-all radiation pattern is thus seen to be a weighted superposition of three X patterns with their symmetry axes 120° apart in the xy plane, plus one Y pattern with symmetry about the z axis. Relative to the z axis, then, the angular distribution is

$$W(\theta=0)=(1/N)[N_XW_X(\theta^*=\pi/2)+N_YW_Y(\theta=0)], \quad (7a)$$

$$W(\theta=\pi/2)=(1/N)[N_X\{W_X(\theta^*=0)+2W_X(\theta^*=\pi/3)\}/3+N_YW_Y(\theta=\pi/2)]. \quad (7b)$$

It is easy to verify that the value of $\{W_X(\theta^*=0)+2W_x(\theta^*=\pi/3)\}$ is independent of the particular choices of θ^* so long as they are related with threefold symmetry; in other words, the superposition of three X patterns with trigonal symmetry is invariant under rotation about the z axis. From Eqs. (7) the anisotropy is computed as in Eq. (6).

To minimize the computational labor, the calculation just outlined was programmed for an IBM 650 digital computer. $H_{\rm int}$ was varied in steps of 10 from zero to 200 oersteds; $1/T$ was also stepped by 10 from zero to 420. The parameters in Table I appropriate to this calculation are those for CZN. Figure 7 is a graph of these results. The ratio $N_X/N_Y=1.6$ for Fig. 7, since this value gives a much better agreement with experiment (Sec. III A) in the high-temperature region ($1/T<100$) than does 1.8.

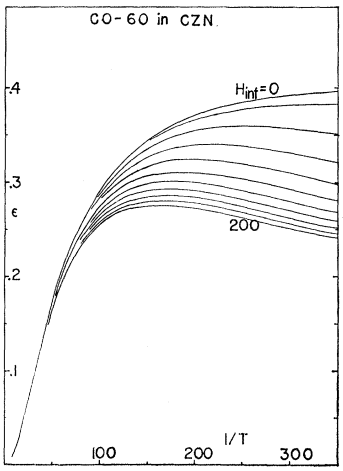

FIG. 7. Anisotropy ϵ of gamma radiation from Co^{60} in Ce-Zn nitrate versus $1/T$ for values of the internal magnetic field $H_{\rm int}$, discussed in the text, from zero to 200 oe in steps of 20 oe. The external field is zero, and $N_X/N_Y=1.6$.

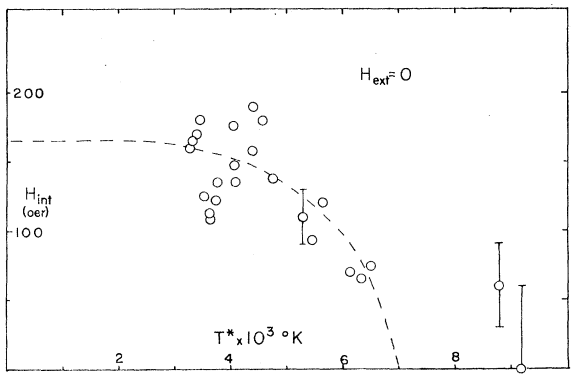

FIG. 8. Magnitude of the internal field, in oersteds, required to account for the anisotropy of gamma radiation from Co^{60} in Ce-Zn nitrate below 0.01°K (Fig. 3). The dashed curve represents the "molecular field" approximation, with parameters $T_c=7\times10^{-3}$°K, $H_0=165$ oersteds.

In order to deduce how $H_{\rm int}$ would have to depend on T in this model, we employed Fig. 7 to interpret the homogeneous sample data (Sec. III A) as follows: each value of $\epsilon(1/T^*)$ in Fig. 3 implies a value of $H_{\rm int}$ read from Fig. 7. Then $H_{\rm int}$ is plotted vs T^* in Fig. 8, which shows only points below 0.01°K because ϵ is relatively insensitive to $H_{\rm int}$ at higher temperatures. A curve constructed by the "molecular field" approximation is included for comparison; that is, $H_{\rm int}$ is proportional in magnitude to the average magnetic moment per cerium ion in the direction of the local ordering axis, which is assumed to vary with T according to the spontaneous magnetization curve of the spin-$\frac{1}{2}$ molecular field theory.[34]

A defect of the molecular field approximation, as well as of the internal field model discussed above, is that long-range order (one $H_{\rm int}$) is assumed while short-range order is neglected. We know of no way to include the short-range order realistically, since the problem would be equivalent to calculating the distribution of values of $H_{\rm int}$ at the various cobalt sites. Nor is our nuclear orientation data extensive or precise enough to show whether an ordered state exists between seven and three millidegrees, as Fig. 8 might seem to suggest.

Principal feature of our proposed model of the effect of magnetic interactions is that cobalt ions are subjected to internal fields, due to cerium ions, which polarize groups of X ions in three directions perpendicular to the crystal axis but do not affect the Y ions. Except

[34] See, e.g., F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 609–10.

for the deficiencies just noted, the plausibility of the internal-field model for interactions rests on crystal structure and magnetic data[14] for CZN. Referring to the curves calculated from this model and compared to the homogeneous sample data in Figs. 3, 4, and 5(a), we see that a satisfactory quantitive fit is provided, using the molecular-field approximation.

B. Comparison with Ce-Mg Nitrate

It is noteworthy that Co^{60} in CZN shows larger gamma anisotropies than CMN under comparable experimental conditions. For example, at $1/T=300$ with $H_{ext}=0$, $\epsilon(CMN)^5=7\%$ while $\epsilon(CZN)=26\%$ (Fig. 3); the ϵ of 60% in 300 oe (Fig. 6) is larger than any reported[2] for CMN, even for 430 oe. Thus we suggest that CZN is more attractive for polarization and alignment of cobalt isotopes than is CMN.

One factor causing smaller anisotropies for CMN must be that $A<B$ for X ions. Hence orientation effects for these ions oppose those for Y ions, in the sense that $W_X(0)>W_X(\pi/2)$ but $W_Y(0)<W_Y(\pi/2)$ even in the absence of internal fields. Though it is reasonable to expect that the internal-field model should be applicable to CMN, we are unable to present to say whether the combination of $A<B$ and H_{int} about 165 oe would be capable of explaining such low values of ϵ as 7%. This is because, when $A\neq B$ as for an X ions in CMN, such an ion would not have cylindrical symmetry with respect to the internal-field direction. A general treatment[35] of the radiation pattern, and diagonalization of the full 22×22 energy matrix would seem to be necessary in that case. The limited amount of data on Co^{60} in CMN presently available[2,5] does not seem to us to justify such an extensive theoretical computation. It is possible that N_X/N_Y is larger in CMN, as suggested by Schroeder.[5]

C. Utility of Layered Samples

Layered samples, which avoid interaction effects in nuclear orientation experiments, appear to have quite limited usefulness, on the basis of our experience. The limitation is imposed by the difficulty of cooling the radioactive layer due to the slow rate of heat transport at low temperatures. The utility lies in the possibility of demonstrating the influence of magnetic interactions when nuclear orientation effects appear attenuated.

D. Gamma Anisotropy as a Thermometric Parameter

The dependences of ϵ on T shown in Fig. 3 for the two samples used in this study demonstrate the limitations of ϵ as a thermometer in the very low-temperature range. If our internal-field model is valid, the magnetic-interaction mechanism produces a rather complicated situation of temperature-dependent X-ion energy levels and multiaxial nuclear spin alignments in a homogeneous specimen. Thus from a theoretical standpoint the situation is rendered sufficiently complex and uncertain to preclude the use of ϵ for Co^{60} in CZN as a simple, direct, and accurate indicator of T.

Again referring to Fig. 3 and the layered sample, it is apparent that the layer makes a poor thermometer for the rest of the sample. Possibly at the lowest temperature, where ϵ exceeds theoretical expectation, one could argue that even larger $1/T$ is indicated; for the reason discussed in Sec. II D, however, such a suggestion would have to be accepted cautiously. Note also that $\epsilon(1/T)$ is exceedingly flat in the most interesting temperature range ($T<0.01$°K). It would be better to determine the T^*-T relation for CZN by the customary calorimetric methods, rather than from nuclear orientation of Co^{60}.

V. CONCLUSIONS

The results of this paper may be briefly summarized, more or less in the order of presentation, as follows:

(1) An experimental demonstration that departure from ideal nuclear orientation behavior of Co^{60} in CZN due to $Ce^{3+}-Co^{2+}$ interactions has been given by comparing a layered sample with a homogeneous sample. The usefulness of layered samples is limited by problems of poor heat transfer.

(2) The observed behavior of a homogeneous sample in zero field can be quantitatively explained with the hypothesis of a temperature-dependent internal magnetic field exerted on the Co^{2+}-ions (particularly X ions) by the Ce^{3+} spin system. The plausibility of the internal-field model is based on crystal structure and magnetic data.

(3) CZN is recommended for nuclear orientation of cobalt isotopes, since it surpasses CMN in the magnitude of gamma anisotropy that can be produced under comparable experimental conditions.

(4) Nuclear orientation of Co^{60} in an applied field of 300 oe appears to be much less sensitive to interactions, though considerable caution should be exercised in attempting to deduce the degree of nuclear polarization from gamma anisotropy.

ACKNOWLEDGMENTS

We want to thank Professor E. I. Shaw for his cooperation in handling the radioactive samples. W. W. Strohm, Jr., and L. K. Edwards assisted in the task of making the measurements.

One of us (R. C. S.) wishes to acknowledge helpful discussions with Professor J. G. Daunt and Professor P. S. Jastram concerning the Ohio State work, and the benefit of critical comments by Dr. N. Kurti.

[35] Outlined by S. R. de Groot and J. A. M. Cox, Physica **19**, 683 (1953).