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ABSTRACT

Differential perturbed angular correlation measurements were made on the 2084-keV state of Ce^{140} in aqueous solution at room temperature and in lanthanum metal both at room temperature and at 77° K. The derived g factor of $\pm 1.014 \pm 0.038$ is compared with Rho's theory and with other experimental values. The advantages of working with metals and at low temperatures are discussed. An upper limit of approximately 200° K is set on the quantity ΔE, where $\Delta E/k$ is the energy spacing between Γ_7 and Γ_8 for Ce^{3+} in La metal. An approximate value of 4.1 ± 0.4 a.u. is derived for $\langle r^{-3} \rangle$ of the cerium 4f electron, using the above upper limit for ΔE.

I. INTRODUCTION

Studies of the hyperfine interactions in the 2084-keV state of Ce^{140} can yield important information about nuclear and atomic structure in this region of the Periodic Table. This state's mean life of 5 nsec[1] makes it inaccessible to all methods except perturbed angular correlations. In this paper we report the results of studies to date using this technique.

The nuclear properties of ${}^{82}_{58}Ce^{140}$ are especially interesting because they are accessible to theoretical treatment. The 82-neutron and 50-proton core can be neglected in calculating the properties of the low-lying states, and BCS theory can be applied to the remaining 8 protons, which would just fill the $g_{7/2}$ subshell in a single-particle model. Rho has carried out such a BCS calculation.[2] Furthermore the calculated g factor of the 2084-keV state is quite different on the BCS theory from any of the single-particle possibilities. The BCS wave function for this state involves a rich mixture of shell-model (quasiparticle) basis functions, and a determination of the g factor constitutes a severe test of this theory.

The atomic properties of Ce are interesting because it has stable 3+ and 4+ oxidation states, with the configurations $4f^1$ and $4f^0$. Comparison of the effective fields for these two states affords the possibility of determining the crucial $\langle r^{-3}\rangle$ hyperfine-structure parameter for the 4f electron. We have obtained an approximate value for this parameter as well as an upper limit for the crystal-field splitting $\Delta E(\Gamma_7 - \Gamma_8)$ for Ce^{3+} in metallic lanthanum.

Sample preparation and descriptions of the measurements are given in Sec. II. In Sec. III the g factor is compared with theory. Crystal-field parameters are discussed in Sec. IV.

II. EXPERIMENTAL

Both the integral and the differential angular correlation methods were used to study the g factor of the 2084 keV state in Ce^{140}. These methods are described thoroughly in the literature.[3] We give below only the particulars of our apparatus and the important details of our data-gathering procedures. For all the work reported here the radioactive parent was La^{140}, and the 329-487 keV cascade (Fig. 1) was used throughout.

A. Sample Preparation

Measurements were made on Ce^{140} in solution and in La metal. The La^{140} was prepared by the reaction $La^{139}(n,\gamma)$, using naturally-abundant La (99.911% La^{139}). Since only the trivalent state of La is stable in aqueous solution the liquid sources were prepared by simply dissolving irradiated La_2O_3 in 3M HNO_3. For the metallic sources, 20-30 mg pieces of La metal were irradiated in an argon atmosphere for 8 min. at a flux of 10^{12} neutrons/cm^2-sec.

B. Integral Angular Correlations

In this method a magnetic field is applied to the source perpendicular to the correlation phase and Larmor premium in the intermediate state is manifest as a phase shift in the correlation pattern. We used this method in early experiments, employing a fast-slow coincidence circuit with a resolving time of 18 nsec. Unfortunately the γ-ray spectrum of La^{140} is quite complicated and there is a considerable amount of coincident radiation at the energies of the two peaks in question. These "background" coincidences, which arise largely from Compton-scattered 1597-keV photons, give an angular correlation pattern that is not rotated. In a preliminary report we gave a g factor of + 1.08 ± 0.10 for the 2084-keV state.[4] Less than half of this probable error interval arose directly from counting statistics; the rest arose from uncertainties in the background correction. In a recent independent re-evaluation of the background correction we obtained a value of +0.99 for the g factor. We are thus led to the conclusion that, even after a substantial experimental effort had been made (over 3×10^5 coincidences were collected), we still had measured the g factor to only about 10%. Longer counting periods would not materially help the situation, because the largest source of error was our inability to correct accurately for background. The apparatus was therefore modified to permit differential measurements.

C. Differential Angular Correlations

In these experiments the apparatus was similar to a conventional fast-slow coincidence circuit, except that a time-to-height converter operating on the overlap principle was substituted for the fast coincidence unit. The 1 × 1-1/2 inch NaI(Tl) gamma-ray detectors were mounted on 30-cm quartz light guides which were in turn secured to Amperex 56 AVP photomultiplier tubes. Energy-sensitive pulses were taken from the fifth dynode and passed through a transistorized shaper and into a cosmic multiple coincidence unit which performed a slow coincidence. Time-sensitive pulses from the anode were limited and passed into the time-to-height converter. The pulses from this unit were sent into a pulse-height analyzer that was gated by the slow coincidence unit. The resultant display was an exponential decay curve with the half life of the intermediate state. Such a curve is shown in Fig. 2. This curve gave a half life of 3.52 ± 0.10 nsec for the 2084 keV state, in good agreement with the values in the literature (Table I).[1,5]

An iron core "C" type electromagnet with a 1/2" pole gap provided a maximum field of 42.0 kG on the sample. For low temperature work pole tips with axial holes were used, allowing a dewar to be inserted without destroying the axial symmetry. The maximum field with these pole tips was only 30 kG. The photomultipliers were shielded from the stray field by two concentric mu metal cylinders and a cold-rolled iron tube. The gain shifted less than 1% for maximum field. A time resolution of 5 nsec for the 329 keV-487 keV settings was measured using annihilation radiation from Na^{22}.

For differential g-factor measurements the counters were set at 135° to one another and coincidence time spectra were taken with the magnetic field directed alternately up and down relative to the correlation plane. The resultant time spectra, denoted by $W_+(t)$ and $W_-(t)$, are exponential curves modulated slightly by the Larmor precession of the intermediate state. These spectra were combined to form the ratio R,

$$R = 2\frac{W_+(t) - W_-(t)}{W_+(t) + W_-(t)} = 3/2\ A_2 \sin 2\omega t \quad , \qquad (1)$$

where A_2 is the coefficient of $P_2(\cos\theta)$ in the unperturbed angular correlation,[6] and ω is the Larmor precession frequency. Equation 1 is applicable to cascades for which the angular correlation is given by $W(\theta) = 1 + A_2P_2(\cos\theta)$.

Three independent runs were made on liquid sources, yielding the results given in Table II. For one of the better runs R is shown in Fig. 3. The final value for the g factor of the 2084 keV state from these data is

$$g = +\ 1.014 \pm 0.038 \quad .$$

In deriving this value we have assumed that the paramagnetic correction for these experiments on liquid samples is zero. This point is discussed below. Lanthanum metal sources were studied by differential angular correlation at 295°K and at 77°K. Derived quantities are included in Table II.

III. THE g FACTOR

Three other time-differential measurements of the g factor of the 2084 keV state of Ce^{140} have been reported.[5,7,8] These are summarized in Table III. The agreement among these four values is fairly good, considering the difficulty of the measurement, although none of the error limits overlap the average value of 1.06.

Cerium-140 has 58 protons and 82 neutrons. Thus it is natural to attribute most of its low-lying excited states to the protons alone, assuming that the neutrons form a closed shell. In fact the proton configuration may be regardes as a closed shell at 50, plus 8 protons. These would be expected, in a single-particle model, to fill the $g_{7/2}$ subshell in the ground state, with the next-lowest $d_{5/2}$ shell empty. On this model the configurations $g^2_{7/2}$, $d^2_{5/2}$, and $g_{7/2}d_{5/2}$ (each coupled to J = 4) might be candidates for the 2084-keV state. The calculated g-factors for these configurations, taken from the experimental values of + 2.7881[9] and + 4.26,[9] respectively, for the magnetic moments of La^{139} and Pr^{141} (to account empirically for configuration mixing) are, respectively, +0.80, +1.71, and + 1.092. Evidently if this model were valid the 2084-keV state would have to be regarded as primarily of $d^1_{5/2}\ g^1_{7/2}$ character. This simple shell-model picture does not predict other properties correctly, however, and we must look elsewhere for wave functions that describe this state.

In the light of the success of the BCS model in accounting for nuclear structure in recent years it seems much more realistic to regard the 2084-keV level as a quasi-particle state. Rho has done so and has made a detailed calculation, using Gaussian forces, for nuclei in the Ce^{140} region.[2] His calculations give g = + 0.92,[10] slightly below the experiment values, for the quasi-particle state $|\Psi\rangle_{4+}$ that he considers best, given by

$$|\Psi\rangle_{4+} \cong 0.30|d^2_{5/2}\rangle + 0.91|g^2_{7/2}\rangle - 0.26|d_{5/2}\, g_{7/2}\rangle \ .$$

Rho's g factor was also calculated using the experimental moments of La^{139} and Pr^{141}. Although Rho's calculation was quite involved it nevertheless included several approximations that are necessary to make such calculations tractable. Thus we feel that the theoretical value of 0.92 represents fairly good agreement with experiment, and that the model is therefore essentially correct. At the same time a discrepancy of about 10% remains. It would take us too far afield to discuss the possibilities for adjusting parameters in the theory in order to produce a g factor larger than +0.92. Rho has discussed this complex problem. It seems doubtful that exact agreement can be obtained without improving the theory somewhat, as opposed to simply adjusting parameters.

IV. HYPERFINE INTERACTIONS

One object of these experiments was to study the "paramagnetic correction" that must often be invoked in angular correlation measurements to account for magnetic hyperfine structure effects arising from interaction of the nucleus being studied with orbital electrons. These effects are usually treated by defining an effective magnetic field $\vec{H}_e$

$$\vec{H}_e = \vec{H}_o + \vec{H}_i \ .$$

Here $\vec{H}_o$ is the external field and $\vec{H}_i$ is a hyperfine field induced by $\vec{H}_o$. For the general case one cannot define a time-independent vector $\vec{H}_i$ having the properties of a magnetic field, because magnetic hfs can be regarded as the interaction of a nuclear moment with a magnetic field only for cases in which certain symmetry conditions are fulfilled. If we regard Ce^{3+} essentially as a free ion, we may take the quantization (z) axis along $\vec{H}_o$ and write

$$H_i = H_N \langle J_z \rangle / J, \tag{2}$$

where H_N is the maximum possible hyperfine field, given by

$$\vec{H}_N = 2\langle r^{-3}\rangle \mu_B N \langle \vec{J} \rangle \quad . \tag{3}$$

Here $\langle r^{-3}\rangle$ is the famous radial integral for the 4f electron, μ_B is the Bohr magneton, and N is a standard factor in hyperfine-structure theory.[11] The parameter $\langle J_z \rangle$ is given by

$$\langle J_z \rangle \cong - \frac{g_J \mu_B J(J+1)}{3kT} H_o \tag{4}$$

in high-temperature approximation. Finally then we may write $H_e = \beta H_o$, with[12]

$$\beta = 1 + \frac{2\mu_B^2}{3kT} \langle r^{-3}\rangle \; N \; g_J \; J(J+1) \tag{5}$$

For Ce^{4+}, which has the electron configuration of the xenon core, $\beta = 1$. For most nonmagnetic metals β would be approximately 1, because the electrons that participate in hyperfine interactions are also in the conduction band, where their properties as fermions lead to an attenuation of their susceptibility by a factor of approximately kT/E_F, where E_F is the Fermi energy. This phenomenon, termed "Pauli paramagnetism," is familiar in metal physics.

In the metallic sources of Ce^{140} in La we expect that the above arguments will not apply because the 4f electron is expected to be associated with the Ce ion core rather than in a conduction band. There is abundant evidence from susceptibility measurements that this is the case for pure rare-earth metals. Thus if we may neglect crystal field effects, the Ce^{140} atom in La metal may be treated as a free trivalent ion. Substituting $N = 48/35$, $g_J = 6/7$ $\langle r^{-3} \rangle = 3.64$ to 4.72 a.u.[13,14,15,16] for Ce^{3+} ($4f^1\ ^2f_{5/2}$) into Eq. 5, we find at $T = 298^\circ$ K $1.35 \leq \beta \leq 1.46$. The experimental value (Table II) is 1.35 ± 0.06. This quantitative agreement provides very good confirmation of the model (Ce^{4+} ion in solution, Ce^{3+} in La). Of course this is hardly surprising, because the cerium atom is expected to be highly ionized after β^- decay of La^{140}, and Ce^{4+} is the highest stable oxidation state of Ce. In aqueous solution it would certainly not be reduced in a few nsec. Lanthanum metal, on the other hand, with its conduction electrons, is about as "fast" a reducing agent as one can imagine. Nevertheless the agreement is very encouraging, because a thorough understanding of the relevant chemistry must precede the determination of a magnetic moment by angular correlation. Cohen, Kaplan, and Ofer[7] have made similar measurements on Ce^{140}; their results for β are in good agreement with ours.

Taking the view now that our expectations about the chemistry of our samples are confirmed, we may proceed to apply the data in Table II to the evaluation of parameters describing Ce^{3+} in La. The methods of angular correlation rotation is especially applicable in this case, for which optical spectroscopic methods are not applicable. Our measurements lead to only rather approximate values of these parameters, but they do demonstrate the applicability of this technique to crystal-field studies.

Lanthanum metal has a structure in which the atoms are stratified alternately in sites of cubic and hexagonal symmetry. The hexagonal sites can be simulated by the elongation of a cube along the 111 axis. Bleaney has shown[16] that for praseodymium metal, with the same structure, the contributions of the hexagonal terms to Stark splitting is small compared with that of the cubic terms. We adopt the approximation that all the cerium ions in the La lattice experience a crystalline field of cubic symmetry.[17] Under a cubic field the $^2f_{5/2}$ level breaks up into a quartet and a doublet. The effective hyperfine field H_e is related to the free-ion field by $H_e = f(x)\, H_N$, where, for the doublet lower in energy $f(x)$ is given by[18]

$$f(x) = \frac{5 + 26\, e^{-x} + (32/x)(1 - e^{-x})}{21 + 42\, e^{-x}} , \qquad (6)$$

where $x = \Delta E/kT$. Here ΔE is the energy spacing between the two Stark states.

It is not possible to calculate ΔE accurately, but we may estimate it by analogy with values obtained for other lattices. White and co-workers found a susceptibility anomaly for Ce in the $LaAl_2$ lattice[18] that indicated an energy gap $\Delta E/k = 200^\circ$ K. Measurements on Ce metal yield a splitting of 200° K.[19] The limiting value of $f(\infty)$ indicates that the doublet is the lower state. Because La has a larger lattice constant than Ce we might expect that $\Delta E/k$ would be slightly lower than 200° K. In Fig. 4 we have plotted β determined for Ce in La metal at 298° K and at 77.3° K, from the data in Table II, against $1/T$. The two curves A and B correspond respectively to $\Delta E/k = 0$ and 200° K. The "best fit" to the data is provided by curve A, but the limits of error are such that we can only set an upper limit of $\sim 200^\circ$ K on $\Delta E/k$. It would be interesting to determine $\Delta E/k$ accurately by extending these measurements to lower temperatures.

Even with out very limited knowledge of the crystal-field splitting we can use the data of Table II, together with Eq. 2-6, to make a tentative determination of $\langle r^{-3} \rangle$ for the 4f electron of Ce in La metal. Assuming $\Delta E = 200$ we obtain $\langle r^{-3} \rangle = 4.1 \pm 0.4$ a.u. For finite values of ΔE the value of $\langle r^{-3} \rangle$ would be somewhat higher.

Theoretical estimates of $\langle r^{-3} \rangle$ for the rare earths have been made by Judd and Lindgren[13] and by Lindgren[14] from spin-orbit coupling constants and by Freeman and Watson from unrestricted Hartree-Fock calculations.[15] Bleaney has compared these with experimental determinations for several rare earths[14,16] and suggested an empirical curve for $\langle r^{-3} \rangle$ vs. atomic number. All of this information is presented graphically, along with our result for Ce^{3+}, in Fig. 5. Our result is not sufficiently accurate to be definitive in extending the empirical curve, but, like the other experimental results, it lies between the two theoretical curves. It is thus a reasonable value, and this lends support to our interpretation of the measurements on Ce^{140} reported here, as well as demonstrating the applicability of angular correlation rotation methods to the determination of such parameters.

Table I. Half life of the 2084-keV state of Ce^{140}.

Cascade studies	$t_{1/2}$, nsec	Reference
329 - 487 keV	3.44(6)	1
329 - 487 keV	3.41(4)	5
329 - 487 keV	3.52(10)	this work

Table II. Summary of results for 2084-keV state of Ce^{140}.

Source	Field (kG)	Temperature (deg K)	$g\beta$	β
La^{3+} sol'n	29.7	298	1.115(95)	(1.00)
"	29.7	"	0.994(59)	"
"	42.1	"	0.998(42)	"
Weighted average			1.014(38)	(1.00)
La metal	30.0	298	1.325(113)	1.31
"	33.95	"	1.376(75)	1.36
Weighted average (see text)			1.361(62)	1.35(6)
La metal	30.0	77	2.07(37)	2.04
"	29.8	"	2.53(23)	2.49
Weighted average			2.40(19)	2.37(20)

Table III. Measured g factors for the 2084-keV state of Ce^{140}.

Method	Result	Reference
Differential + integral	$+ 1.11 \pm 0.04$	5
Differential, less than 1 cycle	$+ 1.15 \pm 0.08$	7
Differential	$+ 0.95 \pm 0.10$	8
Differential + integral	$+ 1.014 \pm 0.038$	this work

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6. For this case A_2 is approximately -0.10. The exact value is unimportant here because there is substantial attenuation arising from the finite resolving time of the counters, etc. Fortunately the differential method relies primarily on a frequency measurement and is relatively insensitive to amplitude. The value of A_2 is discussed in refs. 4 and 5.

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FIGURE CAPTIONS

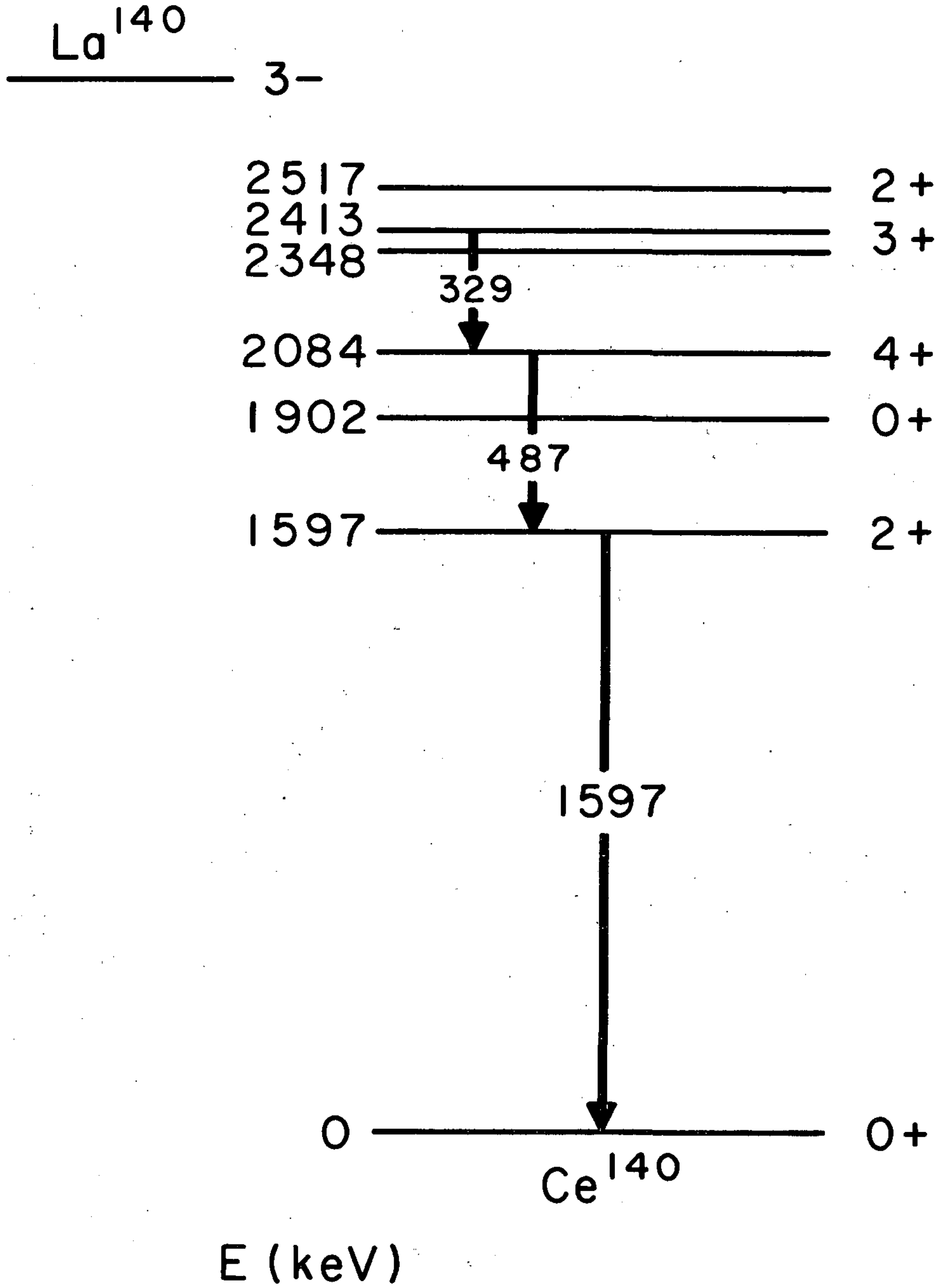
Fig. 1. Partial level scheme of Ce^{140}. The 329-487 keV cascade was used in this work to study the 2084-keV state.

Fig. 2. Prompt resolution curve and decay curve for the 329 keV-487 keV cascade in Ce^{140}.

Fig. 3. Plot of R(t) vs. delay time for the 2084-keV state of Ce^{140} in aqueous solution, in an external field of 42.1 kG.

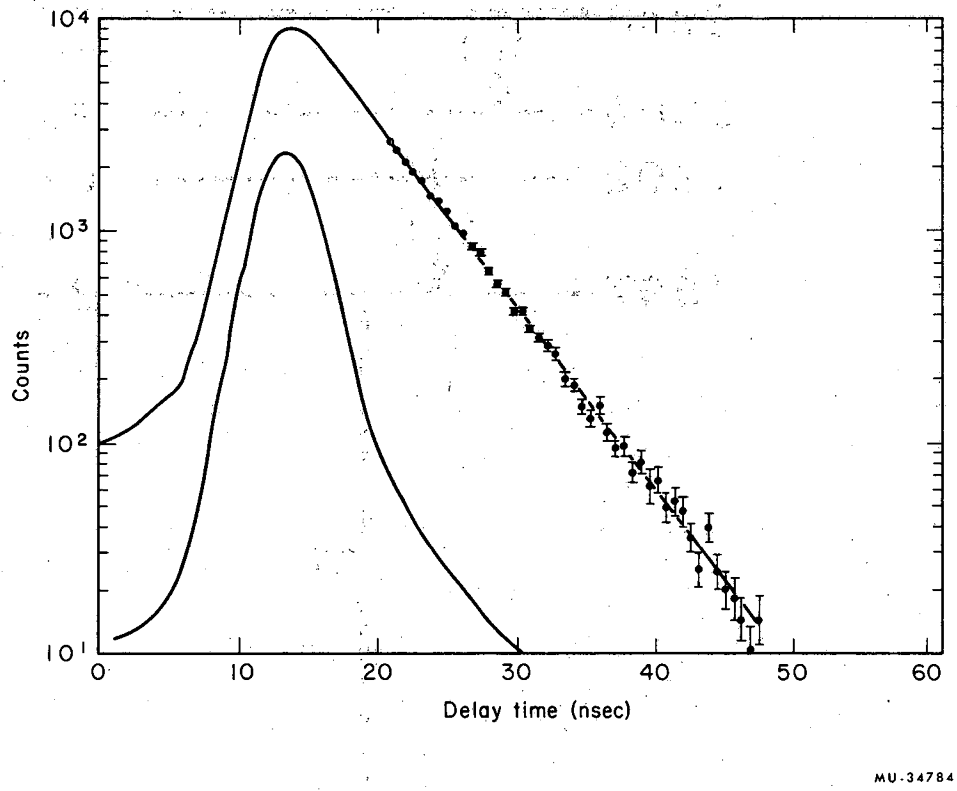
Fig. 4. Paramagnetic correction factor, β, vs. 1/T for Ce^{3+} in La. Theoretical curve A is for free ion; curve B corresponds to $\Delta E/k = 200^{\circ}K$, where ΔE is the crystal-field splitting between Γ_7 and Γ_8, with Γ_7 lowest.

Fig. 5. Plot of $\langle r^{-3} \rangle$ vs. atomic number for rare earths, after Bleaney. Three experimental points are shown and an empirical curve is drawn through them.



MUB-5232

Fig. 1



10⁴
10³
10²
10¹
Counts
0
10
20
30
40
50
60
Delay time (nsec)
MU-34784

Fig. 2

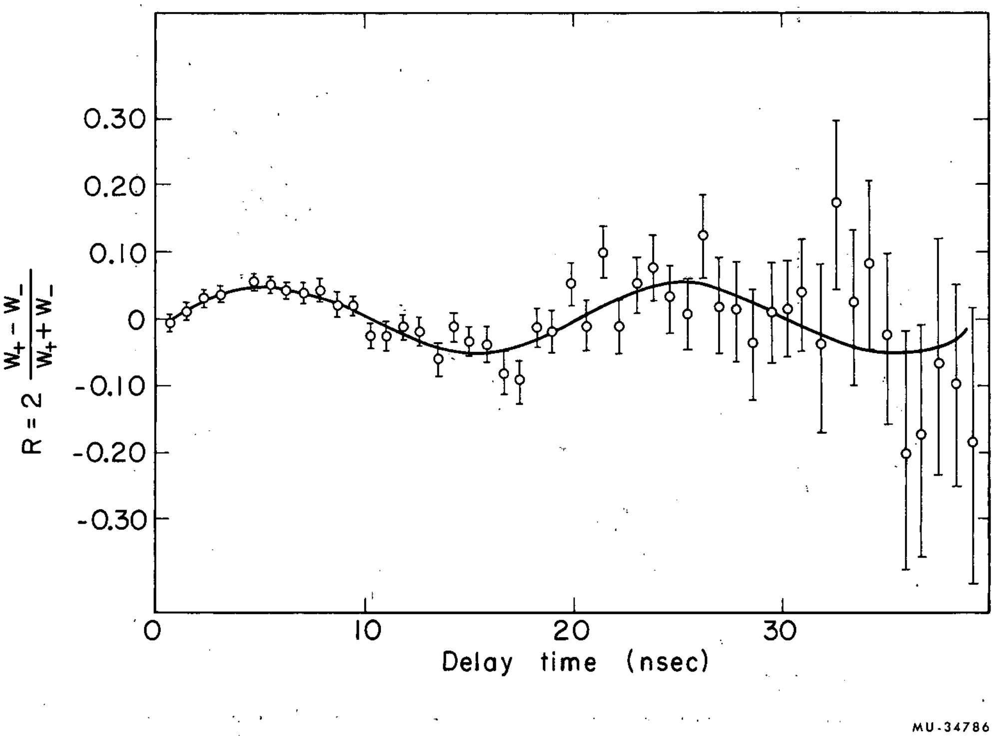
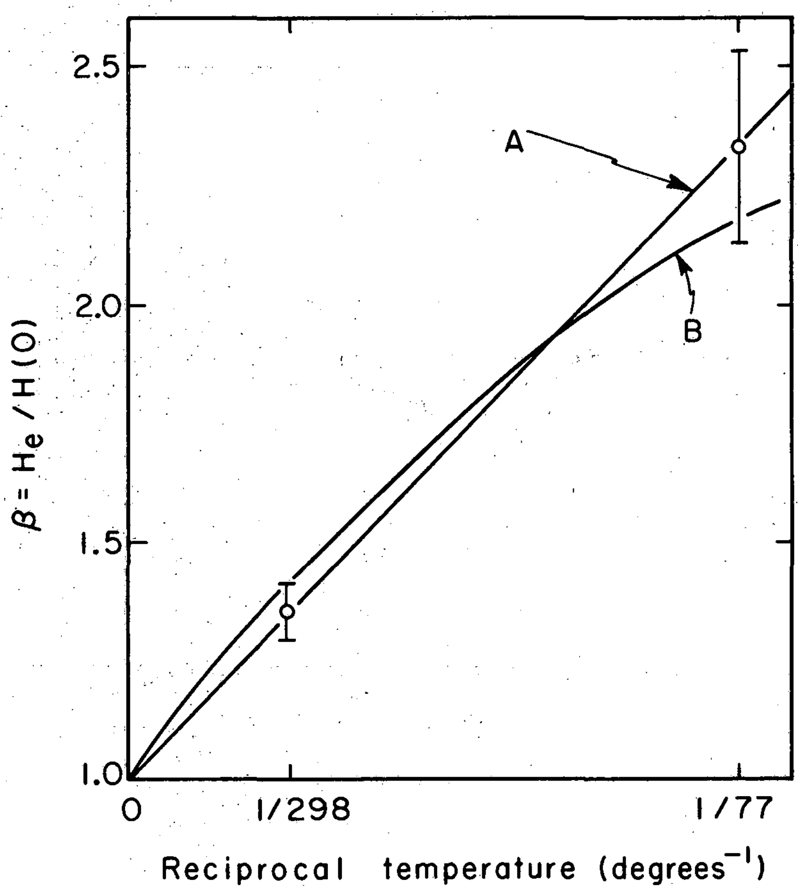

0.30
0.20
0.10
0
-0.10
-0.20
-0.30
R = 2 (W₊ − W₋)/(W₊ + W₋)
0
10
20
30
Delay time (nsec)
MU-34786

Fig. 3



MUB-5233

Fig. 4

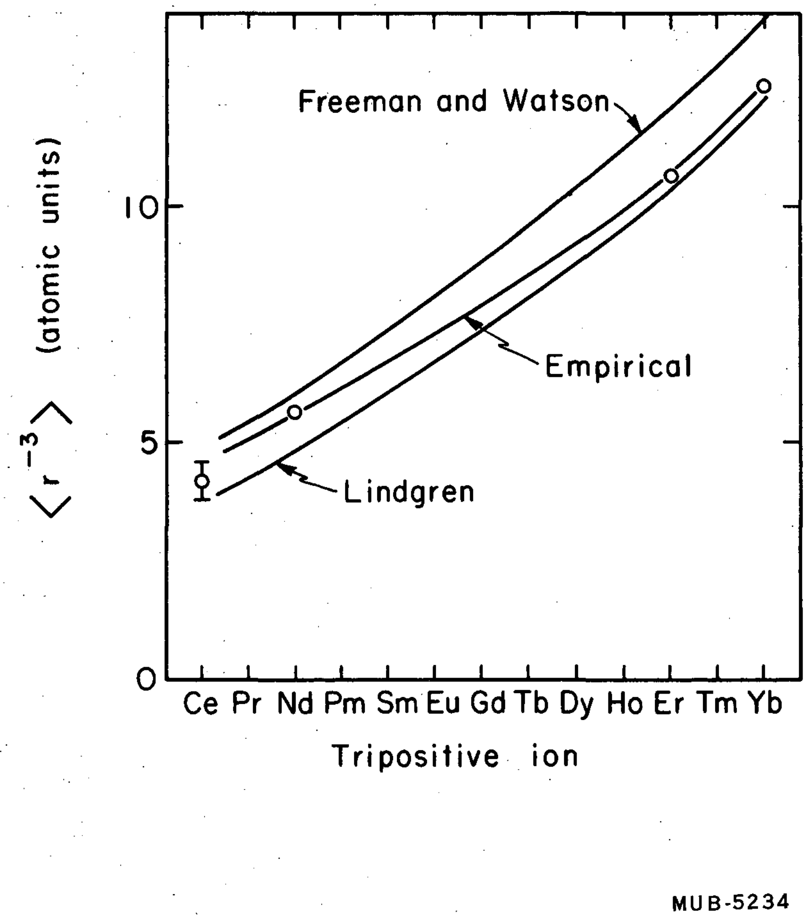

Freeman and Watson
Empirical
Lindgren
10
5
0
$\langle r^{-3} \rangle$ (atomic units)
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb
Tripositive ion
MUB-5234

Fig. 5