much faster with depth, and the region of maximum charge accumulation to be at a smaller relative depth than ours. This is indeed what was observed. However, the region of positive charge for $x \ll 1$ was passed unnoticed, probably because at these energies it is confined to a very thin slice near $x=0$, and it is thus difficult to detect experimentally.

A set of Monte-Carlo calculations were performed recently by Perkins[4] to obtain transmission curves in aluminum for electrons of energies between 0.4 and 4.0 MeV. Although there can be no quantitative comparison between these results and ours, Fig. 2, the curves are qualitatively similar.

ACKNOWLEDGMENTS

The author is indebted to Dr. John S. Laughlin, Division of Biophysics, Sloan-Kettering Institute, for suggesting the general topic and for many useful discussions. The author expresses his gratitude to Professor W. H. Furry, Harvard University, for invaluable suggestions, comments, and encouragement in his capacity as thesis adviser. The valuable aid of William Siler and Frank Ritter in programing parts of the problem for the IBM 7090 computer, and the cooperation of Kenneth King and the Watson Scientific Computing Laboratories and of the The Bendix Computer, Inc., computer group are deeply appreciated.

PHYSICAL REVIEW VOLUME 145, NUMBER 1 6 MAY 1966

Nuclear Magnetic Resonance Studies of Some Materials Containing Divalent Europium*

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(Received 8 November 1965)

This paper reports the results of a low-temperature NMR experiment on Eu^{153} in EuO. The data, which are assumed to be linear with magnetization, are compared with calculated values using spin-wave theory. Values of $J_1/k_b=0.750\pm0.0025$°K and $J_2/k_b=-0.0975\pm0.004$°K are found to give a good description of EuO. This paper also reports the results of NMR studies of the ligands F^{19} and Cs^{137} in EuF_2 and $CsEuF_3$. These experiments indicate that there is a reversal in sign of the unpaired spin density of the europium ion. The same results are obtained with europium-bearing glasses. This effect is discussed in terms of the Freeman-Watson model of Gd^{3+} and in terms of a virtual $5d$ state in Eu^{2+}.

INTRODUCTION

THIS paper presents the experimental results of some nuclear resonance experiments on the Eu^{153} resonance in ferromagnetic EuO and on the Cs^{133}, F^{19}, and B^{11} resonance in some paramagnetic Eu salts and glasses. Since the two experimental techniques are different and since the results given are in a limited sense different they will be discussed separately in the paper. On a more general level, however, the NMR experiment, whether done on the magnetic ion in a ferromagnet or on a ligand in a paramagnet, always measures the local field at the nucleus involved. This local field differs from any external field by the amount of electron-spin polarization at the nuclear site. The electron-spin polarization results ultimately from the amount of unpaired spin on the magnetic ion (the $4f$ electrons of the europium ion in this case). The spontaneous magnetization of a compound results from a favorable alignment of this unpaired spin distribution throughout the crystal. In the magnetic metals the conduction electrons are slightly polarized and bear the magnetic information from atom to atom. In the insulators, such as EuO, there is a polarization of the core which results in the large hyperfine interaction and a polarization of the valence electrons which results in the exchange and thereby the magnetic alignment. By probing with nuclear resonance one learns something about the spatial variation of this polarization of the nonmagnetic electrons.

* Work supported in part by the U. S. Air Force Office of Scientific Research under Contract No. AF 49(638)-1230.

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NUCLEAR MAGNETIC RESONANCE IN FERROMAGNETIC EuO

Uriano and Streever[1] have found the nuclear resonance of Eu^{153} in EuO at 4°K by using the spin-echo technique. They report echoes over a 20 Mc/sec wide frequency range from 125 to 145 Mc/sec with a maximum intensity at a frequency of 138 Mc/sec. The study of this resonance by cw techniques is reported in this paper.

The most striking difference between the two experiments is the cw linewidth which is ≈ 80 kc/sec at 4.2°K. Uriano reports values for T_1 (9×10^{-3} sec) and T_2 (40×10^{-6} sec) obtained from the spin-echo experiment which

[1] G. A. Uriano and R. L. Streever, Phys. Letters **17**, 205 (1965).

are not quite compatible with the cw linewidth. Since there are spin echoes observable over a very wide frequency range one would suppose that there is a very broad distribution of hyperfine interaction in EuO. On this basis the cw experiment will most likely detect a discontinuity in the intensity versus frequency distribution as it does in the case of the octahedral sites in Fe_3O_4 or in lithium ferrite.[2] The cw linewidth reflects the sharpness of the discontinuity rather than the natural linewidth. There is a problem which arises from the symmetry of the magnetic sites in EuO which is face centered cubic. In the case of the ferrites Fe_3O_4 and $Li_{0.5}Fe_{2.5}O_4$ the site symmetry is less than cubic, being either trigonal or axial. The lower symmetry of the ferrites leads to an anisotropic dipolar field which produces the frequency distribution in the nuclear resonance. We go further and compare the line shape observed for EuO with that observed for EuS.[3] The EuO resonance is a single sharp line so strong that at 4.2°K it is easily observed on an oscilloscope with a signal to noise of 20:1 when a single crystal 0.25 cm on a side is used. It has also been followed up to 65°K when the Curie temperature was determined to be 69.35°K from the loading on the oscillator used to detect the resonance. In contrast the EuS resonance contains five distinct lines. Since Eu^{153} has a nuclear spin of $\frac{5}{2}$ the five-line spectrum is believed to result from a quadrupole interaction. In any case the resonance signal from both EuO and EuS is so strong that some mechanism comparable to the domain wall enhancement[4] is necessary to explain coupling between the oscillator and the spin system. Both EuO and EuS have small crystalline anisotropies and large saturation magnetizations. As a result, effects due to demagnetizing fields should be dominant over any other mechanism in determining the domain configuration. Since the structure is cubic, dipolar fields cannot result in an anisotropy hyperfine interaction; this must be found in the magnetic coupling itself.

If we assume that whatever the mechanism is which couples the nuclear spin system to the resonance detector the measured frequency is still proportional to the magnetization of the sample, then we can calculate magnetization versus temperature curves using the spin wave theory as formulated by Charap and compare these with the NMR result. As was done in the case of EuS the magnetic properties were parametrized in terms of an exchange interaction J_1/k_b, a ratio of exchange interactions J_2/J_1, a saturation magnetization $4\pi M$, and an effective field H. Curves of $M(0) - M(T)$ versus T were then calculated and compared with the measured $f(0)-f(T)$ versus T. The best fit obtained is listed in Table I. The parameters which give this fit are

$$J_1/k_b=0.750\pm0.0025\text{°K},$$
$$J_2/J_1=-0.130\pm0.005,$$
$$4\pi M=24\,000\text{ G},$$
$$H=0\pm500\text{ Oe},$$
$$f(0)=138.700\text{ Mc/Sec}.$$

TABLE I. A listing of the experimental data for $f(0)-f(T)$ versus T for the Eu^{153} resonance in ferromagnetic EuO. The calculated $f(0)-f(T)$ are results of a spin-wave calculation using the parameters $J_1/k_b=0.750$°K, $-J_2/J_1=0.130$, $4\pi M=24\,000$ Oe, $H=0$ and $f(0)=138.700$ Mc/sec.

Temperature (°K)	Experimental $f(0)-f(T)$ Mc/sec	Calculated $f(0)-f(T)$ Mc/sec	Difference Mc/sec
2.0940	0.0480	0.0377	0.0102
2.2440	0.0560	0.0462	0.0097
2.5260	0.0690	0.0653	0.0046
2.7640	0.0830	0.0815	0.0014
3.0030	0.1050	0.1006	0.0043
3.1860	0.1200	0.1164	0.0035
3.2450	0.1250	0.1217	0.0032
3.4270	0.1340	0.1386	−0.0046
3.4970	0.1460	0.1454	0.0005
3.5950	0.1540	0.1552	−0.0012
3.6160	0.1550	0.1573	−0.0023
3.7090	0.1660	0.1668	−0.0008
3.8300	0.1740	0.1796	−0.0056
3.9090	0.1900	0.1882	0.0017
4.0700	0.1970	0.2062	−0.0092
4.1750	0.2160	0.2184	−0.0024
20.3000	6.0000	5.9621	0.0378

As is seen in the table there is a systematic deviation of the calculated curve away from the experimental at low temperatures. This may be the frequency pulling as discussed by de Gennes[5]; however, the frequency pulling was not observed in EuS and is expected to be small in EuO.

There is a linear relationship between J_1 and J_2 such that a good approximation of the experimental result may be obtained over a range of values of these parameters. Dalton and Wood[6] give a formula for the Curie temperature of a fcc lattice of spin-$\frac{1}{2}$ ions when there are positive near-neighbor and next-near-neighbor interactions. These formulas modify the Rushbrooke and Wood[7] formula. Two points in the Dalton and Wood calculation make it inapplicable to the case of EuO: the first is that they consider only positive values of J_2, the second is that they consider only spin-$\frac{1}{2}$ ions. Since it is easy, however, a table has been made of values of T_c calculated by the molecular field and the Dalton and Wood methods. It is hoped that changes in the theory of Dalton and Wood necessary to apply it to EuO are slight since it is seen in Table II that the agreement with experiment is very good.

[2] E. L. Boyd, Phys. Rev. **129**, 1961 (1963); E. L. Boyd and J. C. Slonczewski, J. Appl. Phys. **33**, 1077 (1962); S. Ogawa, S. Morimoto, and Y. Kimura, J. Phys. Soc. Japan **17**, 1671 (1962).

[3] S. H. Charap and E. L. Boyd, Phys. Rev. **133**, A811 (1964).

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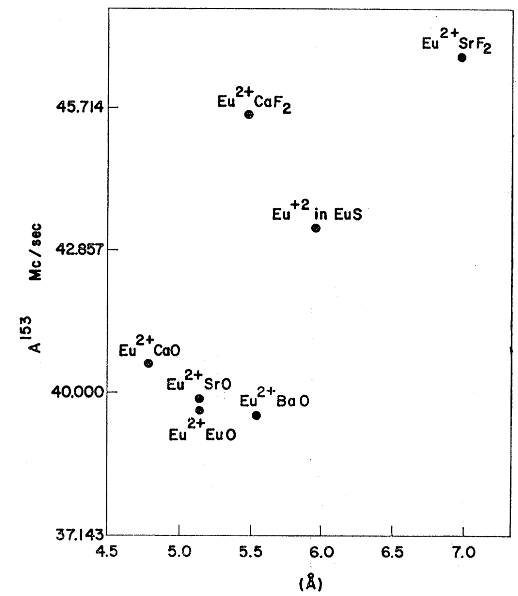

FIG. 1. A plot of the hyperfine constant A in units of frequency versus lattice parameter for Eu^{153} in various environments.

McGuire and Shafer[8] have published a plot of exchange constants versus lattice parameter for the europium chalcogenides. Their values for J_1 and J_2 differ somewhat (especially J_2 which is half the value quoted here) from the spin-wave values. The reason for this difference is attributed first to their use of molecular field theory which tends to underestimate exchange constants and also to their use of a paramagnetic θ value which may be too low.

The hyperfine interaction of Eu^{153} has been studied in several materials and by several workers. Figure 1 contains an epitome of these results. Calhoun and Overmeyer[9] and Gambino and Overmeyer[10] have published values for the hyperfine constants for Eu^{2+} in sixfold coordination in CaO, SrO, and BaO. The SrO is interesting since the lattice parameter is very close to that of EuO. The hyperfine constant A for Eu^{2+} in SrO is nearly the same as that for Eu^{2+} in EuO. The hyperfine constant in the diamagnetic oxide host lattices decreases with increasing lattice parameter. The hyperfine constant increases in the ferromagnetic materials EuO and EuS as the lattice parameter increases, however. In the eightfold coordinated diamagnetic fluorites CaF_2 and SrF_2, the Eu^{2+} hyperfine interaction increases with lattice parameter and is much larger than that in a sixfold coordination (these data are from Shuskus).[11]

TABLE II. A listing of values for the transition temperature of EuO as calculated using various theories and the exchange constants derived from the low-temperature magnetization and spin-wave theory.

M. F. theory	T_c	$\theta = 126J_1/k_b(1+\frac{1}{2}J_2/J_1)$	$=88.3°\pm1°K$
D. W. mean field theory	T_c	$= 99J_1/k_b(1+0.5J_2/J_1)$	$=69.4°\pm0.8°K$
D. W. Green's function	T_c	$= 99J_1/k_b(1+0.68J_2/J_1)$	$=67.6°\pm0.7°K$
D. W. series expansion	T_c	$= 99J_1/k_b(1+0.76J_2/J_1)$	$=67.0°\pm0.7°K$
		measured	69.35°K

The ground state of the divalent europium ion is $^8S_{7/2}$; it has two $6s$ valence electrons and a spin-only moment of $7\mu_b$ due to seven $4f$ electrons which lie within the valence shell. Yet in the compounds EuO and EuS there is a ferromagnetic ordering which appears to be due to direct exchange. Since the $4f$ shells of near-neighbor ions cannot overlap, some other means is needed to carry the magnetic information. By an analysis of the magnetic transition temperatures of the four chalcogenides EuO, EuS, EuSe, and EuTe, McGuire[8] has shown that there is a positive direct-exchange interaction which is greatly distance-dependent and a negative indirect-exchange through the anion which only weakly depends upon the distance between ions. Goodenough[12] has suggested a model in which there is a virtual $5d$ state lying near the ground state which carries the magnetic information via spin polarization much as do the conduction electrons in the magnetic transition metals. Methfessel[13] has extended this model in detail and found much support for it.

Nuclear resonance studies of the anions in compounds of the $3d$ transition metals have proven useful in determining the nature of the wave functions of the $3d$ ions.[14] While the effects upon the anion should be much smaller in the case of Eu^{2+} (in the $3d$ series the $3d$ electrons lie at the outside of the ion and are in direct contact with the anion) they should still be large enough to measure. Neither O^{17} of EuO nor S^{31} or EuS seems promising owing to the low moment and the rare natural abundance of these isotopes.

The isotopes Se^{77} and Te^{125} are good candidates because of their moment and also their abundance which is about 7%. As yet, no nuclear resonance has been observed for either ion in a Eu compound. This is due, most likely, to the present state of the art in the chemical preparation which does not produce homogeneous samples. There are, however, two europium compounds which, while they do not magnetically order, contain easily excited nuclei and in which the europium ion occurs in sites similar to the chalcogenides. These are EuF_2 and $CsEuF_3$. A portion of this paper will discuss the nuclear resonance studies of these two materials.

There also exist a series of paramagnetic glasses in the tertiary system $EuO\text{-}B_2O_3\text{-}Al_2O_3$. While a glass does not have the periodicity of a crystal lattice, the bond

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[9] B. A. Calhoun and J. Overmeyer, J. Appl. Phys. **35**, 898 (1964).
[10] R. J. Gambino and J. Overmeyer, Phys. Letters **9**, 108 (1964).
[11] A. J. Shuskus, Phys. Rev. **127**, 2022, (1962).
[12] J. Goodenough, *Magnetism and the Chemical Bond* (Interscience Publishers, Inc., New York, 1963.)
[13] S. Methfessel, Trans. IEEE (to be published); see also M. W. Shafer, J. Appl. Phys. **36**, 1145 (1965).
[14] See, for example, R. G. Shulman and V. Jaccarino, Phys. Rev. **108**, 1219 (1957).

distances are nearly constant and the bond angles are nearly fixed. Nuclear resonances have been observed for the B^{11} in some of these glasses and will be reported in the following discussion.

NMR STUDIES OF PARAMAGNETIC EuF_2 AND $CsEuF_3$

EuF_2 has the calcium fluorite structure. The distances of interest are the cell edge, 5.85 Å, $Eu^{2+}-F^-$, 2.52 Å and nearest Eu-Eu 4.12 Å. The Eu^{2+} is in a site of eightfold coordination so that the most likely $5d$ orbital is the e_g which projects in the [100] directions.

$CsEuF_3$ has the perovskite structure. The cell edge is 4.77 Å. The Eu-F distance is 2.38 Å. The nearest Eu-Eu distance without an intervening ion is 6.72 Å. The Eu-Cs distance is 4.04 Å. The Eu^{2+} ion is in sixfold coordination, just as it is in EuO, so the most likely $5d$ orbital is the T_{2g} which points along [110] directions.

EuF_2 and $CsEuF_3$ are quite similar magnetically, both having a paramagnetic θ of -5°K. No long-range ordering has been observed in either case. Neutron diffraction does indicate short-range order at 2°K.[15] Lee[16] has reported antiferromagnetic inclusions in EuF_2. Single crystals may be prepared of EuF_2 but no crystal of $CsEuF_3$ has been made. Nuclear resonance has been observed on the F^{19} which has a spin of $\frac{1}{2}$, a moment of 2.6275 nuclear magnetons, and a natural abundance of 100%. Nuclear resonance has also been observed for the $\pm\frac{1}{2}$ transition of Cs^{133} which has a spin of $\frac{7}{2}$, a moment of 2.5642, and a natural abundance of 100%.

Figure 2 is the resonant field shift away from a standard, $CsF\cdot XH_2O$, at fixed frequency versus applied field for the F^{19} in EuF_2 and $CsEuF_3$ and for the Cs^{133} in $CsEuF_3$. The linewidths of the F^{19} in EuF_2 and the Cs^{133} were 25 Oe while the F^{19} in $CsEuF_3$ was ≈ 1 Oe. The lines were symmetrical in the case of $CsEuF_3$ which was a powder sample. The temperature dependence of the shift between 63 and 300°K showed the shifts to be proportional to the magnetic susceptibility. In the case of EuF_2 where a single crystal is available, the shift did not change with change of angle between field and crystal.

The diamagnetic shift of the F^{19} in EuF_2 is in good agreement with the observed isotropic component of the induced hyperfine interaction on F^{19} in CaF_2 with small addition of Eu^{2+}.[17] In view of the cubic symmetry of EuF_2, the anisotropic component should not be observed as indeed it is not. Of more concern are the results of experiments on $CsEuF_3$. This material is complicated by the fact that it contains the most electro-negative ion (F) and the least (Cs). On the other hand, the electronic structure of the Cs^+ is

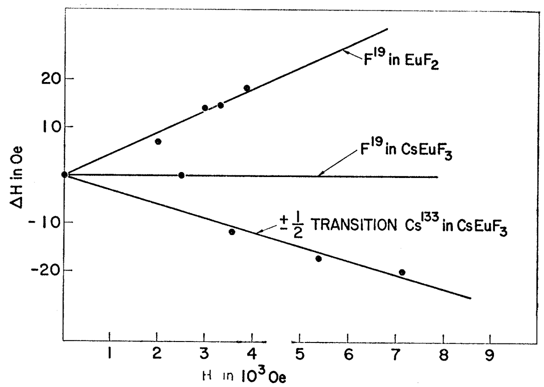

FIG. 2. A plot of the shift in resonant field away from that of CsF hydrated for F^{19} and Cs^{133} in EuF_2 and $CsEuF_3$ versus applied field. These data were taken at 298°K.

identical with that of Eu^{2+} except for the $4f$ shell which is missing. The fluorine line is unshifted which is in agreement with Jaccarino's[18] result for studies of GdF_3. The Cs^{133} resonance shows a strong paramagnetic shift.

Watson and Freeman[19] have calculated the spin density about a Gd^{3+} ion considering all electrons up to $5p$ but not considering $5d$ wave functions. Eu^{2+} is electronically equivalent to Gd^{3+} except that the smaller nuclear charge will permit the electronic wave function to expand slightly in the case of Eu^{2+}. The results of the Watson and Freeman calculation appear in Fig. 3. The general results of the NMR experiment are explained in this figure. The unpaired spin density reverses sign at a radius of 2.0 atomic units going from positive, parallel to the $4f$ spin, to negative, antiparallel, at that radius. This function has spherical symmetry. In the case of EuF_2 the fluorine ion lies well out in the region of negative spin density and has a diamagnetic resonance shift. One can argue that the results of the NMR experiment on $CsEuF_3$ also agree with this model.

The basis of the argument in the case of $CsEuF_3$ is to consider covalency effects of the bonding between europium and fluorine and between the europium and the cesium. The degree of overlap, which is a measure of the covalency, and which determines the hyperfine field, will be different for the two different bonds.

TABLE III. The shift in resonant field for the B^{11} nucleus away from the free ion in several glasses of the composition listed.

Composition in %.			
EuO	B_2O_3	Al_2O_3	% shift
20	80	0	+0.43
20	70	10	−0.45
30	65	5	+0.1
25	50	25	−1.08

[15] Dr. S. Pickart (private communication).
[16] K. Lee, H. Muir, and E. Catalano, J. Appl. Phys. **36**, 1043 (1965).
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[19] S. Greenblatt and P. J. Bray, J. Am. Ceram. Soc. (to be published).

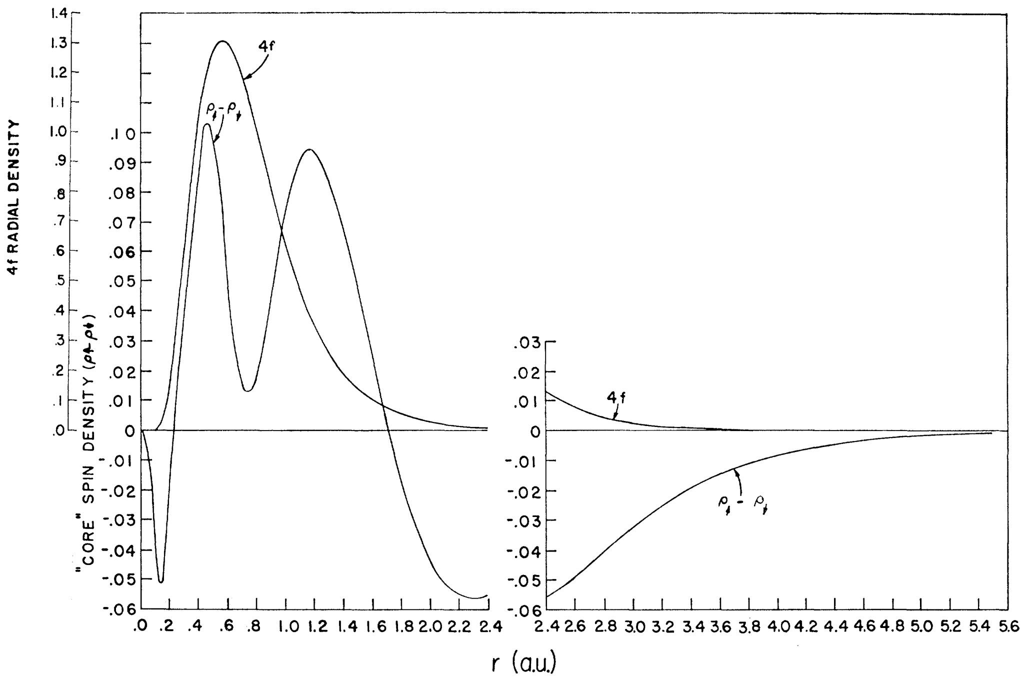

FIG. 3. The computed "core" electron spin density ($p\uparrow - p\downarrow$) for all electrons other than the $4f$ shell and, for comparison, the $4f$ density as well. [After R. E. Watson and A. J. Freeman (Ref. 18)].

The Goodenough model, however, also explains the result since it provides the Eu^{2+} ion with a maximum unpaired spin density along the [111] directions in the case of $CsEuF_3$ and along the [100] direction in the case of EuF_2. In a sense, the two models are the same except that Goodenough specifies the state involved in the bonding.

STUDIES OF GLASSES BEARING Eu^{2+}

The nuclear resonance of B^{11} in glasses made in the EuO-B_2O_3-Al_2O_3 system show much the same effects that were observed in the fluorine compounds. Table III lists the shifts as a function of composition. We again find that the shift goes from diamagnetic to paramagnetic as the average europium to anion (boron) distance increases if the average distance depends upon the aluminum content.

The average bond distance from Eu to B is a function first of the amount of aluminum in the glass and secondly of the coordination of the boron. In the case of the boron coordination, two of the samples are 3 and two are 4 coordinated. The exact location of this line has been the subject of some discussion in the literature. Bray[19] has used the quadrupole splitting of the B^{11} resonance in B_2O_3-Bi_2O_3 glasses as an indication of the change in coordination. The magnetic effect along with the quadrupole splitting in the EuO-B_2O_3 system should be a much better measure of this change. Work should be done to pursue this point.

CONCLUSION

The two types of NMR experiments give a consistent picture of the electronic structure of the Eu^{2+} ion. This picture is in agreement with the Goodenough model which assumes a low-lying $5d$ state which carries the magnetic information from ion to ion. The hyperfine interaction of Eu^{2+} varies greatly with site symmetry and with site size which indicates a large change in the amount of overlap of the core with the $4f$ shell. This is most likely a result of the polarization induced on and the presence of a $5d$ orbital which depends greatly upon the surrounding environment.

ACKNOWLEDGMENTS

The author wishes to thank Dr. M. W. Shafer for the samples, Mrs. Carol Shanesy for the computer program and Dr. Calhoun, Dr. McGuire, Dr. Smart, and Dr. Charap for many discussions of this problem. The author also wishes to thank A. J. Freeman for many discussions on the subject.