A shift for the Ru^{104} curve of $0.012°$ below the Ru^{99} curve, which would be expected if T_{SC} were proportional to the inverse square root of atomic mass, is clearly nonexistent. In fact, the Oak Ridge samples are within $0.001°$ of each other. From the agreement of these isotopes within themselves and with the natural ruthenium, we conclude that less than 10% of the normal isotope shift is present. This is considered as an indication that mechanisms other than electron-phonon interaction may also lead to superconductivity. Mechanisms such as s-d interactions, for instance, have been already recognized in the past for their importance to the superconductivity of the transition elements.[8]

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EXCHANGE POLARIZATION AND THE MAGNETIC INTERACTIONS OF RARE EARTH IONS*

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We are reporting results of a study of the contribution of spin or exchange polarization[1] to the magnetic interaction of a rare earth ion with its neighbors and with its own conduction electrons. This investigation was carried out by means of conventional analytic Hartree-Fock (H-F) calculations[2] for the Gd^{+3} and Gd^{+} ions and a spin-polarized H-F calculation[2] for the Gd^{+3} ion. While the conventional H-F results are of interest in themselves, since they represent the first time such information has been available for the rare earths, we shall only discuss a result of the spin-polarized calculation which may have important consequences for the magnetic behavior of these elements. Our results suggest that the rare earth ions carry a "paired" electron spin density which is underlined negative in their outer reaches. Since the unfilled $4f$ shell electrons are imbedded in the interior regions of the ions, this outer spin distribution can play an important (and perhaps even dominant) role in the magnetic interactions of rare earth ions. In fact, as will be shown, these ions may even appear to their neighbors as having negative spins (i. e., antiparallel to the $4f$ spin direction) and some experimental results are discussed on this basis.

The contribution of "paired" electrons to the magnetic properties of solids has been the object of recent studies[2,3] which have utilized the spin-polarized Hartree-Fock method. Two effects have been studied. The first of these is the contribution of the core s electrons, via the Fermi contact term, to the effective magnetic field at a nucleus in a ferromagnet.[3] This contribution appears to be the dominant source of the recently observed negative effective[4] fields in ferromagnets. Secondly, computations[2,5] for the contribution of the "paired" electron spin density[6] to an

ion's neutron form factor suggest that the contribution is observable, a suggestion which has been borne out by a recent neutron diffraction investigation[7] for NiO. This Letter discusses a third aspect of such spin polarization in solids, namely, its contribution to an ion's magnetic interaction with neighboring ions and conduction electrons. The Gd^{+3} ion's unpaired $4f$ electrons, which are well in its interior, supply an extreme test of the effect. In what follows we presume that the free-ion results are a reasonable description of the Gd "core" electrons in a solid, a not uncommon assumption. The neglect of important relativistic effects, limitations in the spin-polarized formalism,[2] and limitations in computational accuracy for an ion of so high an atomic number make it advisable to view the results which follow for qualitative rather than detailed quantitative behavior.

Figure 1 shows the computed "core" electron spin density $(\rho_\uparrow - \rho_\downarrow)$ for all electrons other than the $4f$ shell and, for comparison, the $4f$ density as well. [Note the change of scales at $r = 3.0$ atomic units (a.u.) to a common scale for both $\rho_\uparrow - \rho_\downarrow$ and the $4f$ density.] The two negative regions indicate densities associated with a spin antiparallel to the net spin of the ion. The region near the nucleus produces the negative effective fields of the type already discussed[3] for iron. The outer region[8] is important for interactions with neighboring atoms and two examples are discussed below.

Nuclear magnetic resonance (NMR) studies[9] in magnetic crystals have revealed large internal magnetic fields at the nuclei of normally diamagnetic atoms like F^-. The hyperfine interactions between the fluorine nucleus and the $3d$ magnetic electrons of the transition metal ion have been interpreted as arising from unpaired spins in the fluoride ion orbitals. This unpairing is thought to arise in either of two distinct ways: (1) because of an admixture of covalent bonding into the purely ionic configuration,[10] or (2) by the unpairing action of the Pauli principle ("Pauli distortion")[11] which affects those fluorine orbitals which have the same spin as the cation $3d$ orbital differently from those orbitals which have opposite spin. In either method the unpaired $2s$ electrons produce an isotropic hyperfine interaction whereas the $2p$ electrons produce an anisotropic interaction, the degree of unpairing being determined by the squares of the overlap integrals, (S^2), between the free F^- orbitals and the $3d$ electrons on the cation. Let us consider the application of this type of analysis to a rare earth salt such as GdF_3 in order to explore the consequences of the negative spin density in the outer region of the Gd^{+3} ion. Since the "paired" orbitals ($5s$ and $5p$) have different radial distributions, they will overlap the fluoride orbitals differently; and it is this <u>difference</u> in their interactions which gives rise to a hyperfine interaction with the fluorine nucleus. Denoting the Gd^{+3} $4f$ shell spin as up (↑), then the extent of the interaction is measured by $S_i^2(\uparrow) - S_i^2(\downarrow)$ where i denotes some pairs of electrons. In Table I we list the squares of the
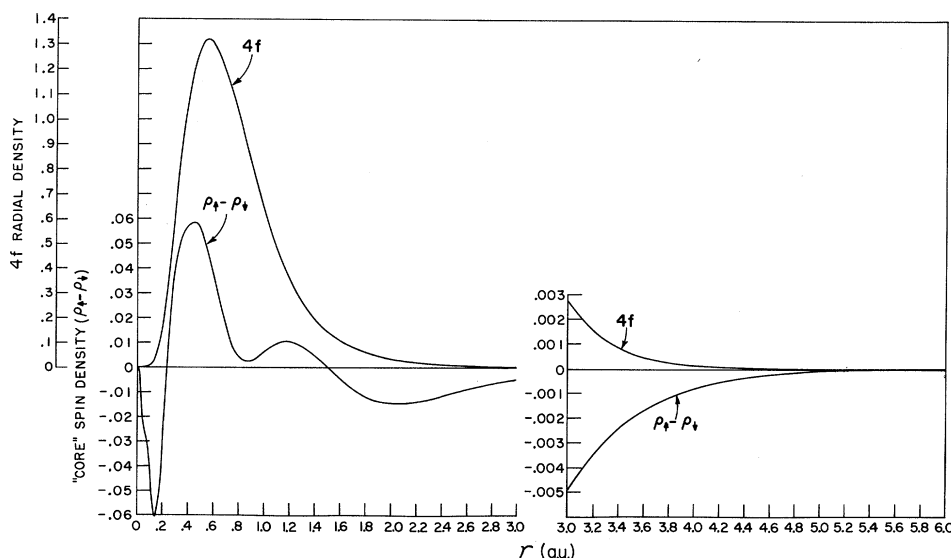

FIG. 1. The computed "core" electron spin density $(\rho_\uparrow - \rho_\downarrow)$ for all the electrons other than the $4f$ shell and, for comparison, the $4f$ density as well. Note the change of scales at $r = 3.0$ a.u. to a common scale for both $(\rho_\uparrow - \rho_\downarrow)$ and the $4f$ spin density. (See <u>Note added in proof</u>.)

Table I. The squares of the overlap integrals, S^2, between the Gd^{+3} outer orbitals and the F^- $2s$ orbital at the nearest neighbor distance of 4.4 a.u., and the net contribution to the internal field at the F^- nucleus $(\sum S_\uparrow{}^2 - \sum S_\downarrow{}^2)$.

	$S_\uparrow{}^2$		$S_\downarrow{}^2$
$4f_\uparrow - 2s$	0.012×10^{-2}		
$5p_\uparrow - 2s$	0.365×10^{-2}	$5p_\downarrow - 2s$	0.483×10^{-2}
$5s_\uparrow - 2s$	0.085×10^{-2}	$5s_\downarrow - 2s$	0.107×10^{-2}
$\sum S_\uparrow{}^2 = 0.462 \times 10^{-2}$		$\sum S_\downarrow{}^2 = 0.590 \times 10^{-2}$	

Net effect $= \sum S_\uparrow{}^2 - \sum S_\downarrow{}^2 = -0.128 \times 10^{-2}$ (equivalent to -7200 gauss at the F^- nucleus). Contribution from the $4f$ shell alone $= +0.012 \times 10^{-2}$ (equivalent to $+700$ gauss).

overlap integrals between the Gd^{+3} $4f(\uparrow)$, $5s(\uparrow$ and $\downarrow)$, and $5p(\uparrow$ and $\downarrow)$ and the F^- Hartree-Fock[12] $2s$ orbital at the observed[13] nearest neighbor distance of 4.4 a.u. [For lack of space the anisotropic $(2p)$ interaction will not be discussed here.] We see that the sum of $S_\downarrow{}^2$ is greater than the sum of $S_\uparrow{}^2$ and that $S_\uparrow{}^2 - S_\downarrow{}^2$ gives an effect which is ten times as large as, and opposite in sign to that obtained by considering the $4f$ overlap alone. In other words, in the context of either the Pauli distortion or covalency mechanisms (2 and 1 above), our spin-polarized functions predict that a Gd^{+3} ion, as seen by a nearest neighbor F^- ion, appears (in its interactions) to have a spin which is antiparallel to the actual Gd^{+3} spin.[14]

Jaccarino et al.[15] have reported the NMR of Al^{27} in the rare-earth intermetallic compounds and have interpreted the observed negative Knight shift as arising via the Ruderman-Kittel-Kasuya-Yosida[16] mechanism from a negative exchange interaction between the localized $4f$ electrons and conduction electrons. We have calculated overlap integrals and simple electrostatic exchange integrals $\langle 1/r_{12} \rangle$ (which are important for direct magnetic interactions) between the Gd^{+3} spin-polarized functions and Hartree-Fock Al wave functions[17] at the observed $GdAl_2$ internuclear distance of 6.2 a.u. The outer region of negative spins again dominates over the $4f$ interaction for both the S^2's and the $\langle 1/r_{12} \rangle$ integrals, i.e., the Gd^{+3} ion again behaves as if it had a negative spin. In fact, these outer "core" electrons account for about one-tenth of the observed Knight shift[15] and their contribution is of the correct (i.e., negative) sign. In the metal the conduction electrons (which have not been included in our calculations) would also have a "paired" negative spin density in their outer regions; and since

their overlap with the Al functions would be greater than that of the "core" functions, their contribution to the hyperfine field at the Al nucleus would also be correspondingly greater. It is, therefore, possible that the observed negative Knight shift could be interpreted as arising from exchange polarization without invoking a negative exchange interaction between the localized $4f$ electrons and the conduction electrons.

We also studied the exchange interaction between a spin-polarized Gd^{+3} ion and conduction electrons in the metal. The "conduction" electrons were assumed to be $6s$ electrons (which we obtained from a conventional and more accurate H-F calculation for the free Gd^+ ion) and exchange integrals were calculated between this $6s$ electron and the spin-polarized Gd^{+3} orbitals. In this case the $4f$ exchange interaction (i.e., between the $4f\uparrow$ and $6s\uparrow$ electrons) was found to dominate over the net exchange interaction (i.e., the difference in exchange between the "core" $\uparrow$ and $\downarrow$ spins with the $6s$ electrons) which was negative and about one-fifth that of the $4f$ electrons, in agreement with Hund's rule for localized interactions.

These investigations and related ones on the magnetic interactions of rare earth ions will be discussed at length in a forthcoming publication.

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Note added in proof. Through an error the $5p$ spin density was not included in the $(\rho_\uparrow - \rho_\downarrow)$ plot shown in Fig. 1. The inclusion of the $5p$ spin density shows a much larger and more extensive negative spin density for large r than that shown in the figure.

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OPTICALLY DRIVEN SPIN PRECESSION

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The possibility of modulating a light beam at rf resonant frequencies by applying rf energy to an optically pumped spin system has been amply demonstrated theoretically[1,2] and experimentally.[3,4] We report here an interesting converse— that of modulating the light source at frequencies close to the Larmor frequency and observing a precessing spin polarization induced by the modulated light. The resulting resonance has quite different characteristics from the usual rf magnetic resonance; in particular, it does not show saturation effects although the linewidth does depend in part on the average intensity of the incident light. This is, to our knowledge, the first time that an rf resonance effect has been produced by means that do not involve variation of a field directly coupling the rf-separated energy states.

The effect may be observed in optically pumpable spin systems such as alkali metal vapors[1,3] or metastable helium[5] by applying circularly polarized resonance radiation at right angles to the magnetic field H_0 (Fig. 1). In an earlier paper[3] we developed a phenomenological treatment of optically pumped spin systems that included the effects of several light beams. If we adhere to the notation of reference 3, and specialize to a single light beam perpendicular to H_0, and no rf field, we obtain the following equations for the spin system:

$$dF/dt + i\gamma H_0 F + F/S_2 = P_x \mathfrak{M}',$$

$$dM_z/dt + M_z/S_1 = 0,$$

where $F = M_x + iM_y$, P_x is the pumping rate of the light, S_1 and S_2 are relaxation times including effects of the light, and $\mathfrak{M}'$ is the equilibrium polarization that would be produced by the light in the absence of a magnetic field and thermal
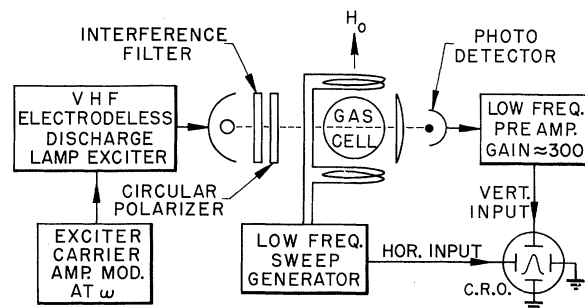

FIG. 1. Block diagram of apparatus. The interference filter is employed in alkali vapor to remove the $S_{1/2} \rightarrow P_{3/2}$ resonance radiation. In the metastable helium experiment no interference filter is used, and a high-frequency electrodeless discharge must be applied across the absorption cell to generate metastables.