θ_A and θ_B we are able to calculate the expected values of the relative intensities of the $\Delta m = 0$ lines. These values ($x = 0.3$ for the A site, 1.6 for the B site) are in good agreement with the fit indicated for the 70-kOe spectrum of Fig. 1(b). Taking into account the presence of iron in the B site, one finds that the spontaneous moment calculated for such a model is equal to $1.3 \pm 0.5\ \mu_B$, which is significantly lower than the moment expected from a Néel model ($3.2\ \mu_B$).[15] Furthermore, the B site moment is dominant in agreement with susceptibility data.[3] We note that the observation of only two hyperfine fields is consistent with both the Yafet-Kittel as well as the Néel model and is therefore not sufficient to distinguish between these models.

We conclude that the magnetic structure of ferrimagnetic $NiFe_2O_4$ is of the collinear Néel type. An example of a Yafet-Kittel structure is shown for the chromium substituted $NiFe_{0.3}Cr_{1.7}O_4$.

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[13] The temperature dependence of the Mössbauer spectrum of $NiFe_{0.3}Cr_{1.7}O_4$ shows evidence of relaxation effects in the paramagnetic and in the ferrimagnetic state [I. Nowik and H. H. Wickman, Phys. Rev. Letters 17, 949 (1966)] from 120°K to ≃500°K ($T_N \simeq 280$°K). Above 120°K, the hyperfine lines broaden and we observe the appearance of a quadrupole doublet which increases in intensity as T increases. The presence of a quadrupole splitting (0.40 ± 0.05 mm/sec) can be attributed to some local distortion of the crystallographic structure mainly for the A sites [T. R. McGuire and S. W. Greenwald, Bull. Am. Phys. Soc. 3, 43 (1958)].

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[15] The moment derived from magnetization curves is about $0.5\ \mu_B$ [Ref. 3 and T. R. McGuire and S. W. Greenwald, Bull. Am. Phys. Soc. 2, 22 (1957)]. However, it has recently been shown [F. Van der Woude, G. A. Sawatsky, and A. H. Morrish, Bull. Am. Phys. Soc. 12, 724 (1967)] that the distribution of the cations in the A and B sites is related to the method of preparation and heat treatment. For a sample with iron in tetrahedral sites only, but with the same θ_A and θ_B as for our sample, the theoretical moment would be $1.0 \pm 0.5\ \mu_B$.

SPIN POLARIZATION NEAR LOCALIZED MOMENTS IN METALS*

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Following the treatment by Ruderman and Kittel[1] of magnetic interactions between nuclear magnetic moments in metals, Yosida[2] showed that localized moments in a metallic environment couple with a long-range oscillatory interaction. This interaction arises from the conduction-electron spin polarization

$$\vec{S}_e(r) = A\frac{\sin 2k_F r - 2k_F r \cos 2k_F r}{(2k_F r)^4}(g-1)\vec{J}, \qquad (1)$$

caused by the magnetic ions, with A a positive constant and g the Landé g factor for the moment with angular momentum $\vec{J}$.[3] Blandin[4] has suggested a different form from the spin polarization: Rather than being caused by the exchange interaction between conduction electrons and magnetic ions, the spin polarization results from the different screening requirements imposed on spin-up and spin-down conduction electrons by the localized moment.

Provided that the screening phase shifts at the Fermi surface are not a multiple of π, a spin polarization is found which again decreases asymptotically as $\cos 2k_{\mathrm{F}}r/r^3$, and which has a larger amplitude than the Ruderman-Kittel-Yosida (RKY) polarization.

Rare-earth solutes have particularly interesting properties because spin-orbit coupling dominates the impurity angular momentum structure even in a metallic host.[5] If, in metallic solution, $\vec{L}\cdot\vec{S}$ coupling reproduces the free-ion magnetic properties, impurity orbitals can be identified individually as occupied or unoccupied. A phase-shift description then involves 14 distinct f-wave phase shifts each of which must be zero or π at the Fermi surface. Two consequences follow: First, the residual resistivity due to f-wave scattering vanishes, and second, the spin polarization which varies asymptotically as $\cos 2k_{\mathrm{F}}r/r^3$ also vanishes because states at the Fermi cutoff have no density disturbance.

The disturbed density may be written[6]

$$\delta\rho(r)=\int_0^{k_{\mathrm{F}}}\rho_k(r)\big[(n_3{}^2(kr)-j_3{}^2(kr)\sin^2\eta_{lm} - n_3(kr)j_3(kr)\sin 2\eta_{lm}\big]|Y_{lm}(\theta,\varphi)|^2 \qquad (2)$$

for screening of an f orbital with quantum numbers l and m. If the f level is narrow and symmetrical, the integration may be effected using asymptotic forms of the Bessel functions to give the result for large r:

$$\delta\rho(r)=\rho_{k_1}(r)\varphi(\omega r)\frac{\cos 2k_1 r}{r^2}|Y_{lm}(\theta,\varphi)|^2, \qquad (3)$$

where k_1 is the center of the f level and ω is the bandwidth through which η rises from 0 to π. The function $\varphi(\omega r)$ depends on the f-level shape, but in all cases cuts off at $r\sim\omega^{-1}$. For Lorentzian and square f levels, $\varphi(\omega r)$ is proportional to $\exp(-\omega r)$ and $j_0(\omega r)$, respectively.

Gardner and Flynn[6] have shown how the average spin polarization $\langle S_e(r)\rangle$ caused by magnetic impurities in liquid-metal solvents may be obtained from measurements of the solvent Knight shift. In this Letter we report measurements on liquid aluminum containing rare-earth impurities and show that the results can be explained by spin-splitting of $4f$ levels which are degenerate with the conduction band. These $4f$ levels appear to have a width of 0.6 eV and a splitting of 0.9 eV between sub-bands of opposite spin.

Earlier workers have studied spin polarization in lanthanide compounds.[7] Jaccarino et al. found that results obtained from $\mathrm{Al_2R}$ compounds could be interpreted in terms of a uniform polarization caused by s-f exchange only if a negative exchange effect was involved. This is contrary to the sense expected from Hund's rules. More recently, Borsa et al. have obtained a similar anomalous result, using the full RKY treatment, from studies of $\mathrm{Sn_3R}$ compounds. In all cases the exchange interaction deduced varies inexplicably among the rare-earth elements. The present results could also be interpreted in terms of a negative, variable exchange coupling, whose magnitude is, moreover, considerably larger than that derived from measurements on pure rare-earth metals.

The molar susceptibilities of $4f$ impurities (other than Pm) have been measured in the temperature range 700-1100°C for alloys of concentration ≤ 2 at.% rare earth. The observations are in generally good agreement with spin-orbit theory for free ions[8] in the configurations listed in Table I. All solutes except Eu and Yb are in the configurations expected for trivalent ions. Both Eu and Yb are approximately divalent.

Observed values of $\Gamma=K^{-1}\partial K/\partial c$, with K the Knight shift, are shown in Fig. 1. In interpreting these results we suppose that spin-up f states in lighter rare-earth impurities lie at the Fermi surface, while for those rare earths heavier than Gd, the spin-down states lie at the Fermi surface and the spin-up states lie at some lower k value, k_1. From an extension of the analysis in Ref. 6, one may show that for narrow, square f bands in a free-electron gas,

$$\Gamma=\frac{1}{7}\left\{\frac{2\langle g(g-1)J(J+1)\rangle}{3}+\frac{2\chi_{HF}kT}{N\mu_{\mathrm{B}}{}^2}\right\}\frac{\omega}{4kT}\left\{\frac{k_1}{k_{\mathrm{F}}}A_3(k_1)\frac{S_l}{S}\cos\theta_l+A_3(k_{\mathrm{F}})\frac{S_u}{S}\cos\theta_u\right\}, \qquad (4)$$

with ω the width of the impurity spin bands, now expressed in energy units. In Eq. (4), the quanti-

Table I. Knight shifts and linewidths caused by rare-earth impurities in liquid Al at 1000°C.

Element	Configuration	S	L	J	Γ	ω(eV)
La	$4f^{0}$	0	0	0	-1.07 ± .10	-
Ce	$4f^{1}$	1/2	3	5/2	-.64 ± .06	.74 ± 0.07
Pr	$4f^{2}$	1	5	4	0	.57 ± 0.06
Nd	$4f^{3}$	3/2	6	9/2	+.91 ± .09	.74 ± 0.07
(Pm)	$4f^{4}$	2	6	4	-	-
Sm	$4f^{5}$	5/2	5	5/2	-3.42 ± .34	1.36 ± 0.14
Eu	$4f^{7}$	7/2	0	7/2	-11.8 ± 0.6	.49 ± 0.05
Gd	$4f^{7}$	7/2	0	7/2	-13.6 ± 0.7	.57 ± 0.06
Tb	$4f^{8}$	3	3	6	-12.8 ± 0.6	-
Dy	$4f^{9}$	5/2	5	15/2	-11.0 ± 0.6	-
Ho	$4f^{10}$	2	6	8	-8.8 ± 0.4	-
Er	$4f^{11}$	3/2	6	15/2	-5.7 ± 0.3	-
Tm	$4f^{12}$	1	5	6	-3.2 ± 0.1	-
Yb	$4f^{14}$	0	0	0	-1.1 ± 0.1	-
$\mathrm{L_u}$	$4f^{14}$	0	0	0	-.59 ± .02	-

ties $S_u \cos\theta_u$ and $S_l \cos\theta_l$ are the projections of the upper and lower sub-band spins, $\vec{S}_u$ and $\vec{S}_l$, respectively, on the total ionic spin $\vec{S}$. From the cosine rule one finds

$$\frac{S_u}{S}\cos\theta_u = \frac{(|n_u - n_\theta)(n_u - n_l| + 2) + n_u(n_u + 2) - n_l(n_l + 2)}{2(|n_u - n_l|)(|n_u - n_l| + 2)},$$

and

$$\frac{S_l}{S}\cos\theta_l = \frac{(|n_u - n_l|)(|n_u - n_l| + 2) + n_l(n_l + 2) - n_u(n_u + 2)}{2(|n_u - n_l|)(|n_u - n_l| + 2)}, \tag{5}$$

with n_l the number of occupied states in the lower energy band and n_u the number of occupied states in the upper energy band. We have also introduced

$$A_3(k) = 7\int_0^\infty [n_3^2(kr) - j_3^2(kr)]D(r)dr, \tag{6}$$

with $D(r)$ the radial distribution function giving the density of solvent sites surrounding an impurity.[9] χ_{HF} is the impurity susceptibility attributed to off-diagonal matrix elements; it is known as the high-frequency contribution.

La and Lu, while having no unbalanced f electrons, nevertheless each cause a small change in Knight shift due to s-, p-, and d-wave screening. We have allowed for similar valence scattering effects of magnetic impurities by interpolation between the values of Γ for La and Lu. One obtains the bandwidth ω of Eq. (4) from Knight-shift data for those rare earths with ≤7 $4f$ electrons. A reasonable value is $\omega = 0.6$ eV (see Table I). The expression (4) then provides a good fit to the remaining data when $k_1/k_F A_3(k_1) = 0.89 A_3(k_F)$, which implies that k_1

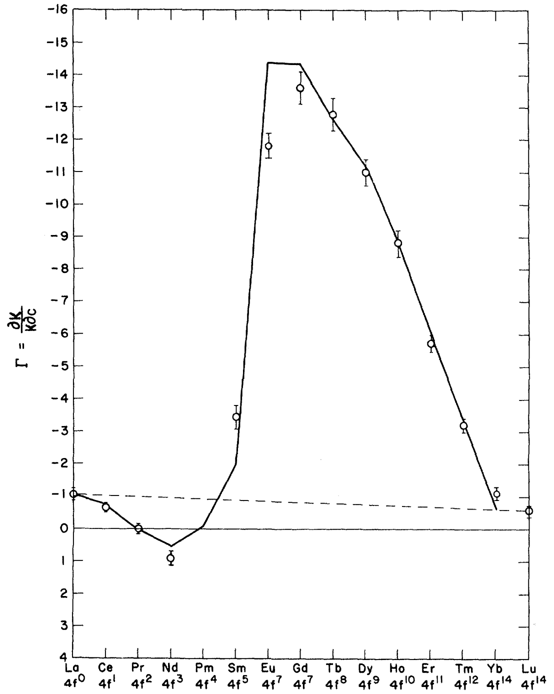

FIG. 1. Experimental values of $\Gamma = K^{-1}\partial K/\partial c$ for rare-earth solutes in aluminum. The solid line shows the theoretical Γ when the $4f$ bandwidth is 0.6 eV (square band) and the splitting is about 1 eV. The broken line shows the assumed baseline caused by s, p, and d wave scattering. The theoretical curve has been adjusted to the baseline.

$= 0.96k_F$. The splitting in energy units between the spin-up and spin-down bands is then $E = E_F(1 - k_1^2/k_F^2) = 0.9$ eV. The solid line in Fig. 1 is calculated from (4) using the above values of the width and splitting of the impurity bands. It is assumed for convenience that the density of states, in k space, of an impurity band is square. The variation with solute species does not depend on the choice of band shape. As a point of physical understanding, it may be noted that the magnetic contributions to Γ from light and heavy rare earths are of opposite sign because $\vec{S}$ is parallel to $\vec{J}$ for heavy rare-earth elements but antiparallel for the light elements, in accordance with Hund's rules. Thus the Knight shift provides direct insight into the impurity angular-momentum structure.

If the exchange interaction is presumed to be constant among the lanthanides, then RKY theory can give a fair account of the relative Γ caused by different solutes. For lighter impurities, the variation with solute is identical with that of the narrow-band treatment, but for elements heavier than Gd, the two theories diverge by some 20%, the present treatment being correct essentially within the experimental uncertainties (Fig. 1). A more serious difficulty is the size of exchange interaction necessary to account for the present results. It can be shown that for an exchange interaction Γ_{ex}, the Knight shift change is given by

$$\Gamma = -\pi Z \Gamma_{ex} J(J+1) g(g-1) A_R / kT, \tag{7}$$

with Z the valence, and

$$A_R = \int_0^\infty (2k_F r \cos 2k_F r - \sin 2k_F r)(2k_F r)^{-4} D(r) dr. \tag{8}$$

We may estimate A_R for a typical close-packed liquid radial distribution function to be $\simeq -5 \times 10^{-3}$, although it may be somewhat smaller because of the size difference between rare-earth and Al ions. This value may be compared with -3×10^{-3} obtained by Borsa et al.[7] for the sum over Sn sites in trivalent Sn_3R compounds. On substituting parameters for Gd in Eq. (7), one obtains $\Gamma_{ex} = -1.0$ eV, or $\Gamma_{ex}V \simeq -30$ eV Å^3, which is not easy to reconcile with the value of 5.7 eV Å^3 needed to explain the Curie temperature of pure Gd.[3]

In contrast to these unsatisfactory conclusions, the narrow-band result does not appear unreasonable. The bandwidth indicates a lifetime $\sim 10^{-14}$ sec for electron-core collisions, which is sufficient for spin-orbit coupling to be established, and an order of magnitude longer than the lifetime of $3d$ core states in Al.[10] The splitting appears to be very small for lanthanide ions, but is roughly equal to that of the magnetic $3d$ ions when dissolved in Cu.

Finally we emphasize that the present conclusions are restricted to rare-earth ions in Al. The structure of magnetic ions doubtlessly depends on the solvent electron gas; we expect that RKY and narrow-band treatments are applicable in different ranges of solvent structure. Further experimental and theoretical results concerning these regimes are being obtained in our laboratories and will be reported in due course.

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INVERSION ASYMMETRY EFFECTS ON OSCILLATORY MAGNETORESISTANCE IN HgSe[†]

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A beat frequency in the oscillatory magnetoresistance of zincblende HgSe is interpreted as arising from the inversion-asymmetry splitting, which is shown to be about 0.007 eV at the Fermi level appropriate to 1×10^{18} electrons/cm^3.

The space group of the diamond lattice has an inversion symmetry operation which requires that $E(\vec{k})$ be twofold degenerate for all $\vec{k}$. The zincblende lattice results from replacing the two group-IV atoms of the diamond lattice basis with one group-III atom and one group-V atom (or a group-II and a group-VI atom), and the inversion symmetry is lost. If the zincblende material has a finite spin-orbit splitting, $E(\vec{k})$ will no longer be twofold degenerate at a general value of $\vec{k}$. Although the theoretical existence of this inversion-asymmetry splitting has been recognized for some time,[1] the small size of the splitting has made it difficult to observe experimentally. Recently, Robinson[2] reported results of cyclotron resonance on p-type InSb which, he argued, required the inversion-asymmetry splitting for interpretation. In this Letter we propose that the Shubnikov–de Haas (SdH) measurements of Whitsett[3] on n-type HgSe quite strikingly demonstrate these zincblende splittings. We first rule out another possible explanation of Whitsett's results and then show how to find the orbits which give the SdH frequencies. An interesting situation occurs when the magnetic field, $\vec{B}$, is parallel to a $\langle 100\rangle$ direction. The $\langle 100\rangle$ zero-field orbits are quenched by magnetic-field-induced splittings in a fashion which is the reverse of magnetic breakdown. By comparing the SdH frequencies with those computed from the theoretical E vs $\vec{k}$ we find values of the inversion-asymmetry splitting for HgSe.

Whitsett's results show that the conduction-band cross-sectional area is only weakly dependent on the direction of $\vec{B}$ with respect to the crystalline axes, as expected for a band with a minimum at $\vec{k}=0$. However, at electron concentrations of $\sim 1\times10^{18}$ cm^{-3} and higher, a beat frequency is found for $\vec{B}$ along all directions in the $(1\bar{1}0)$ plane except $\langle 110\rangle$. These effects are reproducible from sample to sample and we have verified Whitsett's results in our laboratory.

Although the details of the HgSe band structure have not been conclusively established, it is expected that the conduction band was either p-like Γ_8 symmetry as α-Sn or s-like Γ_6 symmetry as InSb, and it is possible to treat these two cases together. Kane has found the energy for either a Γ_6 or Γ_8 band to be[4]

$$E^{\pm}=E'+(\hbar^2/2m_0+a^2A'+b^2M+c^2L')k^2+(b^2-2c^2)(L-M-N)f_1(\vec{k})\pm\sqrt{2}\,ab\beta f_2(\vec{k}),\quad(1)$$