tion decreases less rapidly with x, probably reflecting the onset of Ni-Ni interactions.

These data provide strong evidence for the existence of itinerant electrons with localized magnetic moments. Several questions remain unresolved: the nature of the magnetic state in a random solid solution at concentrations lower than one cobalt in every nearest neighbor on the average; the absence of an exchange-enhanced susceptibility; the decrease in μ_S for $0.95 < n < 1.0$; and the unusually large Weiss constant for solid solutions containing nickel. It appears, however, that magnetic systems such as the one described here provide a unique opportunity to study ferromagnetism unencumbered by the complexities of conventional ferromagnetic metals.

We wish to thank D. B. Rogers for many helpful discussions.

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HIGH-DEGREE EXCHANGE INTERACTION BETWEEN RARE-EARTH IONS

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(Received 21 June 1968)

From the EPR spectra of pairs of Ce^{3+} and Nd^{3+} ions in $LaCl_3$ and $LaBr_3$ it is possible to isolate contributions to the interaction tensors from high-degree anisotropic superexchange interaction of the form $J_+^5(1)J_-^5(2)$ and $J_z^l(1)J_\pm^5(2)$.

Recently there has been a considerable amount of theoretical speculation concerning the possibility of anisotropic interactions of high degree in the angular momentum operators between ions whose orbital moments are not quenched.[1-5] These interactions may arise either from the electrostatic coupling between the electric multipole moments of the two atoms or from a more general form of exchange interaction in which one allows the exchange coupling to depend on the orbitals involved. With a few notable exceptions,[6,7] however, there is almost no detailed experimental information available on such systems. In this Letter we report new measurements on the interactions between the ground-state doublets of Ce^{3+} pairs in $LaBr_3$ and Nd^{3+} pairs in $LaCl_3$ and $LaBr_3$,[8] using the technique of EPR of pairs of coupled ions. In addition, we present a reanalysis of some previous results on Ce^{3+} pairs in $LaCl_3$.[9] By making a detailed comparison of the g tensors and interaction tensors for both the nearest-neighbor (nn) and next-nearest-neighbor (nnn) pairs in all four systems it is possible to isolate contributions from superexchange terms of the form $J_+^5(1)J_-^5(2)$ and $J_z^l(1)J_\pm^5(2)$. We believe that this is the first explicit measurement of such high-degree terms. In addition it is found that there is unambiguous evidence for electric quadrupole-quadrupole (EQQ) interaction between the Ce^{3+} ions, and that the higher-rank electric multipole interaction (EMI) terms are significantly smaller than the EQQ.

The total spin Hamiltonian for a pair of identical Kramers doublets in a magnetic field $\vec{H}$ is given by:

$$\mathcal{H}_{ij} = \mu_B \vec{H} \cdot g \cdot \vec{S}_i + \mu_B \vec{H} \cdot g \cdot \vec{S}_j + \vec{S}_i \cdot K_{ij} \cdot \vec{S}_j, \quad (1)$$

where $\vec{S}_i$ and $\vec{S}_j$ are effective spin-$\frac{1}{2}$ operators. Using EPR one can measure the g tensor and the traceless part A of the tensor K. The components of these tensors which we were able to measure in the experiments, carried out mainly at 36 Gc/sec and 4.2°K, are summarized in Table I. In certain cases, values for the additional components of K may be deduced by combining the pair results with the measured bulk properties of the concentrated material.[10] In particular, such an analysis for Ce^{3+} gives K_{zz}^{nnn}

Table I. Experimental results for Ce^{3+} and Nd^{3+} in $LaCl_3$ and $LaBr_3$. The difference between the pair and single-ion g values, $\Delta g = g(\text{pair}) - g(\text{single ion})$ are given, together with the traceless interaction tensors. The nnn tensors are only determined up to a rotation through an integer multiple of 60° about the z (c) axis. The errors are typically 3 in the last decimal place quoted.

	Ce^{3+} in						Nd^{3+} in					
	$LaCl_3$[a]			$LaBr_3$			$LaCl_3$			$LaBr_3$		
Δg_{nn}	-0.01			-0.01			-0.053[b]			-0.057		
		-0.01			-0.01			-0.053			-0.057	
			+0.004			+0.003			+0.022			+0.070
A_{nn}	-0.071			-0.109			-0.208[b]			-0.286		
		-0.071			-0.109			-0.208			-0.286	
			+0.142			+0.217			+0.416			+0.572
Δg_{nnn}	0.00	--	0.065	+0.01	--	0.052	0.005	-0.009	-0.002	0.001	-0.008	-0.007
	--	0.00	0.000	--	+0.01	0.023	-0.009	0.007	0.002	-0.008	0.019	0.017
	--	--	0.00	--	--	0.00	-0.002	0.002	-0.004	-0.007	0.017	-0.004
A_{nnn}	0.001	--	0.00	±0.001	--	-0.061	0.103	0.001	-0.039	0.074	0.028	-0.042
	--	0.001	0.00	--	±0.001	-0.038	0.001	0.067	-0.002	0.028	0.094	-0.006
	0.00	0.00	-0.003	-0.061	-0.038	±0.002	-0.039	-0.002	-0.170	-0.042	-0.006	-0.168

[a]Ref. 9.
[b]Ref. 8.

$\approx \frac{1}{2}(K_{xx}^{nnn} + K_{yy}^{nnn}) = -0.083 \pm 0.015$ cm^{-1} in $LaCl_3$,[10] and -0.10 ± 0.02 cm^{-1} in $LaBr_3$.[11] As we shall see later, the presence of these sizable terms in $K_{xx}^{nnn}, K_{yy}^{nnn}$ is very significant.

Superexchange between two ions has usually been written

$$\mathcal{H}_{12} = \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j, \tag{2}$$

where $\vec{S}_i$ and $\vec{S}_j$ are real rather than fictitious spin operators for electrons i and j associated with ions 1 and 2, respectively. More generally one may allow for the orbital dependence of the exchange integral by describing the interaction for two ions within a given L, S, J manifold with the Hamiltonian[1,2]

$$\mathcal{H}_{12} = \sum_{\substack{ll' \\ mm'}} g_{ll'}^{mm'} \tilde{O}_l^m(J_1) \tilde{O}_{l'}^{m'}(J_2), \tag{3}$$

where l, l' take values from 1 to 7 and $l + l'$ is even. The Hamiltonian describing the EMI[9,3] or the virtual phonon exchange (VPE)[4,5] has the same form, but l and l' are restricted to values 2, 4, and 6 (for EQQ, $l = l' = 2$). In the present cases we estimate the VPE to be several orders of magnitude too small to make significant contributions to either K or g. The magnetic dipole-dipole interaction can also be expressed in the same form with $l = l' = 1$, but in this case the $g_{ll}^{mm'}$ may be calculated from the known g values and crystal structure. Although of similar form, the various interaction mechanisms contribute in different orders of perturbation theory to the measurable g and K tensors of pairs in the lowest Kramers doublet of the manifold. This enables one to isolate the contribution from certain terms. Terms with odd l, l' (i.e., magnetic dipole-dipole and superexchange) can contribute in first order to K, but those with even l can contribute only in second and higher orders. All terms may contribute in second order with

the Zeeman term to g. Such interaction-induced g shifts must, however, be distinguished from shifts due to a local distortion of the crystal field caused by replacing a neighboring La^{3+} by a smaller rare-earth ion.

The wave functions describing the ground Kramers doublet of Ce^{3+} and Nd^{3+} in $LaCl_3$ (and to a very good approximation, $LaBr_3$), necessary for calculating the first-order matrix elements of $\mathcal{H}_{12}$, are given in Table II. One notable difference between the states of Ce^{3+} and those of Nd^{3+} in the lowest manifold is that those for Ce^{3+} are almost pure $|J, M_J\rangle$ while those for Nd^{3+} are not. This feature greatly restricts the number of sizable matrix elements for Ce^{3+}, and enables us to draw conclusions about Ce^{3+} which we cannot draw about Nd^{3+}. We now consider the experimental results in terms of the above interactions.

For Ce^{3+} the EQQ interaction contributes only to $g_{xz}{}^{nnn}$ and $g_{yz}{}^{nnn}$. From Table I it may be seen that these are in fact the only two sizable components of the measured Δg so that it appears quite likely that this mechanism is responsible. The contribution of EQQ in Nd^{3+} is calculated to be two orders of magnitude smaller, and thus is negligible. Higher order EMI are expected to contribute in a general way to g for the Ce^{3+} pairs, so that the absence of other components in the g tensor indicates that their effect is negligible. Similarly, the small g shifts observed for the Nd^{3+} nnn pairs shows that the higher order EMI are insignificant there as well. In reality, the Nd^{3+} g shifts almost certainly arise mainly from a local distortion of the crystal field. The contributions from distortions to g shifts in Ce^{3+} are expected to be much smaller than those for Nd^{3+} because of the better fit of the Ce^{3+} ion into the lattice; hence they are most certainly negligible in comparison with the measured $g_{xz}{}^{nnn}$ and $g_{yz}{}^{nnn}$. Finally, simple order-of-magnitude calculations based on the measured interaction tensors show that superexchange could not possibly account for the observed Ce^{3+} g shifts. Hence this analysis of the g shifts isolates the EQQ interaction in Ce^{3+} and shows that higher degree EMI are negligible in comparison.

Table II. Ground-state wave functions expressed in terms of $|J, M_J\rangle$.

Ce^{3+} in $LaCl_3$ and $LaBr_3$[a]	$0.998\left\|\frac{5}{2}, \mp\frac{5}{2}\right\rangle \mp 0.063\left\|\frac{7}{2}, \pm\frac{7}{2}\right\rangle \mp 0.011\left\|\frac{7}{2}, \mp\frac{5}{2}\right\rangle$
Nd^{3+} in $LaCl_3$ and $LaBr_3$[b]	$0.936\left\|\frac{9}{2}, \pm\frac{7}{2}\right\rangle + 0.351\left\|\frac{9}{2}, \mp\frac{5}{2}\right\rangle$

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EQQ contributes negligibly to K for Nd^{3+}. For Ce^{3+} it contributes only to K_{zz} in second order, since any of the other components of K involve $\Delta M_J = 5$. Therefore, for both Nd^{3+} and Ce^{3+} it is necessary to postulate superexchange to account for the observed K.

For Nd^{3+} superexchange terms of all odd ranks in $\mathcal{H}_{12}$ contribute to each element of K in first order, so that it is not possible to separate them out. For Ce^{3+} pairs, on the other hand, because of the fact that the ground doublet is almost pure $\left|\frac{5}{2}, \pm\frac{5}{2}\right\rangle$, it is possible to make an unambiguous deduction: We can isolate terms of fifth rank in the interaction. The argument may be outlined as follows. Terms of first and third rank contribute mainly to the K_{zz} alone, via the components $\mathcal{J}_{ll'}{}^{00}$. They can only contribute to the other terms in K, via components with m or $m' = \pm 1$, through the small admixtures of the $\left|\frac{7}{2}, \pm\frac{7}{2}\right\rangle$ states, and totally unreasonable values of the exchange interaction energy would be necessary to account for the measured values of these terms. That this is so may be seen by considering $K_{xx}{}^{nnn}$ as an example. To explain the observed value of $-0.083\ cm^{-1}$ in $LaCl_3$ we would require a matrix element of the term $\mathcal{J}_{ll'}{}^{1-1}$ of $\sim 5\ cm^{-1}$, and this is at least 20 times the magnitude expected from an extreme extrapolation to our case from the measured mean single-electron exchange matrix element determined from Gd^{3+} pair measurements.[12] Furthermore the Nd^{3+} pair results indicate no such anomalously large terms. We therefore see that the presence of large K_{xx} and K_{yy} terms, and the off-diagonal nnn K-tensor components, can only be due to the presence of fifth-rank exchange interaction terms which can couple states with $\Delta M_J = \pm 5$ directly. There will no doubt be lower rank terms also present, but we cannot isolate these. The only term in $\mathcal{H}_{12}$ contributing directly to K_{xx} and K_{yy} is $\bar{O}_5{}^{+5}(J_1)\bar{O}_5{}^{-5}(J_2)$, whereas the K_{xz} and K_{yz} terms must arise through terms of the form $\bar{O}_l{}^0(J_1)\bar{O}_5{}^{\pm 5}(J_2)$.

We conclude, therefore, that the observed terms in $K_{xx}{}^{nnn}$, $K_{yy}{}^{nnn}$, $K_{xz}{}^{nnn}$, and $K_{yz}{}^{nnn}$ for Ce^{3+} pairs in $LaCl_3$ and $LaBr_3$ are clear and

unambiguous evidence for sizable high- (fifth-) rank superexchange terms as predicted theoretically by Levy, and Elliott and Thorpe. It is apparent that such terms are by no means unique to the Ce^{3+} ion and must be anticipated in most situations where the magnetic moment contains an appreciable orbital contribution.

We would like to thank Dr. R. Shore and Mrs. C. Peagram for growing the crystals used in this study. We would also like to thank Dr. P. M. Levy, Dr. W. P. Wolf, Dr. R. J. Elliott, and Mr. R. B. Clover for a number of helpful discussions.

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NEW PHOTOEMISSION STUDIES OF THE *d* BANDS OF NICKEL AND COPPER

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(Received 17 June 1968)

New photoemission studies of the optical density of states of nickel and copper are reported. In contrast to other earlier measurements, both Ni and Cu have a sharp maximum at the top of the *d* band. The *d*-band optical density of states of Ni and Cu are consistent with a simple rigid-band model: The exchange splitting of Ni is estimated as $\delta E_{ex} \simeq 0.4 \pm 0.2$ eV.

Previous photoemission studies[1-3] of the optical density of states of Ni have found an anomalously strong peak at 4.5 eV below the Fermi level E_F. The observation of this strong peak is contrary to all one-electron band calculations (which are becoming increasingly successful in explaining numerous properties[4,5] of Ni). The conclusion was that a rigid-band model was not valid for the *d*-band optical density of states of Ni and Cu.

We report new photoemission results for Ni and Cu which differ from those previously published.[1,3,6,7] The most striking results of the new measurements are (1) the observation of a sharp maximum in the density of states at the top of the filled *d* band for both metals (for Ni at E_F and for Cu ~2 eV below E_F) and (2) a large reduction in the amplitude of the above-mentioned 4.5 eV peak in Ni. We find good agreement between our *d*-band optical density of states of Ni and Cu using a simple rigid band model with an exchange splitting of 0.4 ± 0.2 eV for Ni. In contrast to previous photoemission results, we find general agreement with one-electron band calculations. In particular, we observe good agreement between the optical density of states of Ni and the one-electron band calculations of Hodges, Ehrenreich, and Lang,[4] who determined an exchange splitting of 0.37 eV at E_F. The previously reported[1-3] anomalous peak 4.5