Table I. High-temperature susceptibility coefficients for cubic lattices.

n	a_n
	Face-centered cubic lattice
1	8
2	58.6667
3	413.8667
4	2855.3481
5	19 415.8527
6	130 694.4263
7	873 209.9636
8	5 800 796.3979
	Body-centered cubic lattice
1	5.3333
2	24.8889
3	114.7259
4	509.7877
5	2249.9706
6	9779.9445
7	42 335.1558
8	181 758.3614
	Simple cubic lattice
1	4
2	13.3333
3	43.3778
4	136.2963
5	424.5446
6	1301.5034
7	3967.8674
8	11 998.0391

where x_c corresponds to the Curie temperature. In the ratio method it is convenient to use the equation (Domb and Sykes[4])

$$n[x_c a_n / a_{n-1} - 1] \rightarrow \gamma - 1 \text{ as } n \rightarrow \infty.$$

Both methods suggest $\gamma \sim 1.36$ for all three lattices, the critical temperatures being given by $x_c \sim 0.1572$, 0.2425, and 0.346, respectively. It certainly appears that γ for this classical model is less than for the spin-$\frac{1}{2}$ Heisenberg model (see Ref. 3) and it looks as if it is rather greater than the value $\frac{4}{3}$ suggested by Domb and Sykes[5] and Gammel, Marshall, and Morgan.[6] But there is sufficient uncertainty on this latter point to warrant the computation of further terms in the series.

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[1] H. E. Stanley and T. A. Kaplan, Phys. Rev. Letters 16, 981 (1966).

[2] G. S. Rushbrooke and P. J. Wood, Mol. Phys. 1, 257 (1958).

[3] G. A. Baker, H. E. Gilbert, J. Eve, and G. S. Rushbrooke, Phys. Letters 20, 146 (1966).

[4] C. Domb and M. F. Sykes, J. Math. Phys. 2, 63 (1961).

[5] C. Domb and M. F. Sykes, Phys. Rev. 128, 168 (1962).

[6] J. Gammel, W. Marshall, and L. Morgan, Proc. Roy. Soc. (London) 275, 257 (1963).

TEMPERATURE VARIATION AND SEPARATION DEPENDENCE OF EXCHANGE INTERACTIONS OF Gd^{3+} PAIRS IN $LaCl_3$*

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(Received 10 June 1966)

Gd^{3+} pairs in $LaCl_3$ provide examples of comparable magnetic and exchange interactions for which precise values of the interaction constants can be found from microwave resonance fields. The separation dependence of the exchange is estimated from the observed temperature variation and found to be anomalous.

The measurement of exchange interactions from the epr of pairs of coupled ions is now well established. In most previous experiments[1] the exchange constants have been derived from the temperature variation of the intensity of transitions within groups of states separated by a dominant exchange interaction. However, when the exchange interactions are small and comparable with other effects, such as the magnetic dipole coupling, there is mixing between states in different groups, and accurate values of the interaction parameters can then be obtained from the positions of the pair resonance lines.[2] In this Letter we show how such measurements may be used to obtain precise information about the exchange interactions between nearest- and next-nearest-neighbor pairs of Gd^{3+} in $LaCl_3$, and their variation with temperature. The measurements also yield precise values of the effective magnetic dipole-dipole interactions, from which the mean pair separation at various temperatures may be deduced. It is thus possible to measure the variation of the individual exchange parameters as a function of the mean interionic distance, without having to rely on compressibility or thermal-expansion data.

The experiments were performed on a sample of $LaCl_3$ containing 1% Gd^{3+} (and 1% Ce^{3+} to reduce the relaxation time at low temperature). The crystal structure of $LaCl_3$ is hexagonal (space group $C6_3/m$) with C_{3h} point symmetry at the rare-earth sites,[3] and it is isostructural with $GdCl_3$. The nearest neighbors (nn) lie along the c axis 4.375 Å apart (4.105 Å in $GdCl_3$), and the next-nearest neighbors (nnn) are 4.843 Å apart (4.721 Å in $GdCl_3$), with the bond axis making an angle of 63.2° with the c axis. As will be shown later, the Gd^{3+} pair ions take up positions intermediate in separation between those of $LaCl_3$ and $GdCl_3$.

The spin Hamiltonian for a pair of Gd^{3+} ($^8S_{7/2}$) ions is given quite accurately by a Zeeman term, isotropic exchange and magnetic-dipole interaction terms, and three axial crystal field terms[4]:

$$\mathcal{H}_{12} = g\mu_B H_z(S_{z1}+S_{z2}) + J_{12}(\vec{S}_1\cdot\vec{S}_2) + \alpha_{12}[\vec{S}_1\cdot\vec{S}_2 - 3S_{z1}\cdot S_{z2}] + \sum_{i=1,2}\left[\frac{b_2^0}{3}O_{2i}^0 + \frac{b_4^0}{60}O_{4i}^0 + \frac{b_6^0}{1260}O_{6i}^0\right],$$

where the magnetic field and the axis of quantization have been taken along the pair axis. The magnetic dipole coefficient α_{12} is $g^2\mu_B^2/r_{12}^3$, where r_{12} is the pair separation. For a given pair there are $8\times 8 = 64$ energy levels, all of which are occupied above 20°K, and they give rise to between 50 and 100 epr transitions of sufficient intensity to be detected in our X- and K-band spectrometers. From the form of the Hamiltonian, it is evident that the pair transitions will be symmetric about the center of the spectrum and independent of frequency. These are important clues in separating out the pair lines.

Since the dipolar interactions can be calculated approximately from the lattice spacing and the g value, and the crystal field effects are known to be small[5] (~0.001 cm^{-1}), the only major unknown is the exchange interaction. The analysis then reduces to identifying observed lines as due to a given pair (this is explained fully elsewhere[6]), finding the value of J which gives approximately the same spectrum, correlating the observed lines with specific transitions, and finally varying the five spin-Hamiltonian parameters to fit the spectrum. Figure 1 shows typical sets of observed and calculated line positions and intensities for nn and nnn pair spectra. For both cases the fit is excellent, with rms deviations of 4 and 18 G, respectively,[7] compared with over-all splittings of up to 4000

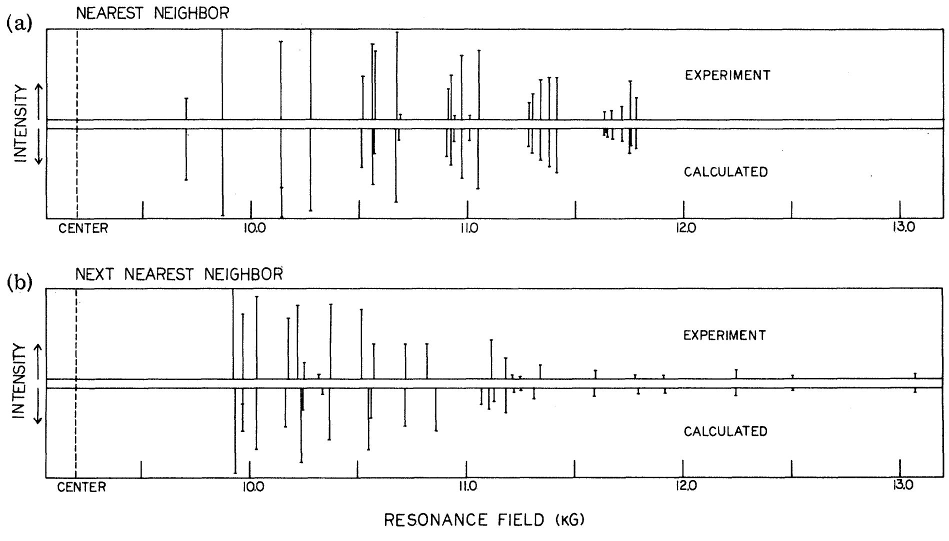

FIG. 1. Experimental and calculated nn and nnn pair spectra of Gd^{3+} in $LaCl_3$ at $T = 77°K$, $\nu = 25.625$ Gc/sec. The figure shows only the high-field halves of the spectra, which are symmetrical about the center ($g = 1.9915$). (a) $J = 0.01333\ cm^{-1}$, $\alpha = 0.02193$, $b_2^0 = -0.00201$, $b_4^0 = 0.00021$, and $b_6^0 = 0.00002$. (b) $J = -0.05950\ cm^{-1}$, $\alpha = 0.01586$, $b_2^0 = -0.00288$, $b_4^0 = -0.00008$, $b_6^0 = 0.00005$.

G and linewidths of ~10 G. The accuracy of the fits precludes important contributions from biquadratic exchange and distortion effects, and it enables one to detect changes in $J_{\rm nn}$ and $J_{\rm nnn}$ of about 0.0001 cm^{-1} and 0.001 cm^{-1}, respectively.

Given this relatively high accuracy, it is straightforward to study the variation of the spin-Hamiltonian parameters as a function of temperature, and such measurements have now been made between 20 and 360°K. Over this temperature range the more intense lines in both spectra move by about 40 G, and some of the smaller nnn lines which are extremely sensitive to the exchange interaction move by as much as 500 G. The results of the experiments are summarized in Table I.[8] It may be seen that all the parameters vary smoothly with temperature, confirming the consistency of the different fits. The variation of the two exchange constants with temperature is shown in Fig. 2(a). Above 150°K the curves are approximately linear, with gradients

$$\left(\frac{1}{J}\frac{dJ}{dT}\right)_{\rm nn} \sim -1.8\times10^{-4}(^\circ{\rm K})^{-1}$$

and

$$\left(\frac{1}{J}\frac{dJ}{dT}\right)_{\rm nnn} \sim 4.3\times10^{-4}(^\circ{\rm K})^{-1}.$$

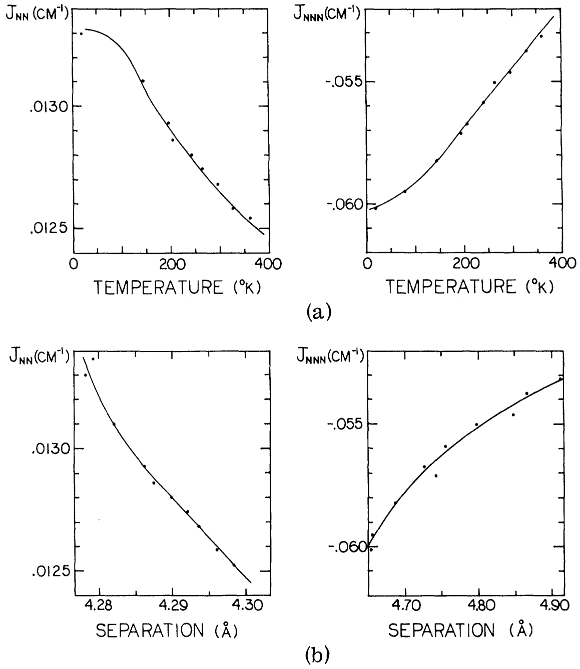

FIG. 2. (a) Exchange interaction versus temperature for nn and nnn pairs of Gd^{3+} in LaCl$_3$. (b) Exchange interaction versus pair separation, r, for nn and nnn pairs of Gd^{3+} in LaCl$_3$, where the r's are calculated from the measured dipolar constants $\alpha = g^2\mu_{\rm B}{}^2/r^3$.

These are somewhat larger than previous estimates [(1 to 2)×10^{-4}] for various ferric-oxide garnets and spinels based on analyses of bulk measurements.[9] The dipolar constants $\alpha_{\rm nn}$ and $\alpha_{\rm nnn}$ also vary with temperature, but much more slowly, with gradients

$$\left(\frac{1}{\alpha}\frac{d\alpha}{dT}\right)_{\rm nn} \sim -0.5\times10^{-4}(^\circ{\rm K})^{-1}$$

and

$$\left(\frac{1}{\alpha}\frac{d\alpha}{dT}\right)_{\rm nnn} \sim -0.7\times10^{-4}(^\circ{\rm K})^{-1}.$$

Table I. Temperature dependence of exchange and dipolar constants for nn and nnn pairs of Gd^{3+} in LaCl$_3$.

Temperature (°K)	$J_{\rm nn}$[a] (cm^{-1})	$\alpha_{\rm nn}$[b] (cm^{-1})	$r_{\rm nn}$[c] (Å)	$J_{\rm nnn}$[d] (cm^{-1})	$\alpha_{\rm nnn}$[e] (cm^{-1})	$r_{\rm nnn}$[f] (Å)
20	0.013 30	0.021 93	4.278	−0.0602	0.015 87	4.765
77	0.013 33	0.021 91	4.279	−0.0595	0.015 86	4.766
145	0.013 10	0.021 87	4.282	−0.0582	0.015 82	4.769
195	0.012 93	0.021 81	4.286	−0.0571	0.015 78	4.774
207	0.012 86	0.021 79	4.287	−0.0567	0.015 79	4.773
243	0.012 80	0.021 75	4.290	−0.0559	0.015 76	4.776
265	0.012 74	0.021 72	4.292	−0.0550	0.015 72	4.780
295	0.012 68	0.021 69	4.294	−0.0546	0.015 67	4.785
329	0.012 58	0.021 65	4.296	−0.0538	0.015 65	4.787
361	0.012 54	0.021 62	4.299	−0.0532	0.015 61	4.791

[a] All values ±0.000 10 cm^{-1}.
[b] All values ±0.000 03 cm^{-1}.
[c] All values ±0.002 Å.
[d] All values ±0.0010 cm^{-1}.
[e] All values ±0.000 05 cm^{-1}.
[f] All values ±0.003 Å.

There are two possible effects which can contribute to the observed temperature dependences: (1) thermal expansion of the lattice as a whole and (2) changes in particular phonon amplitudes. In a soft material such as $LaCl_3$ ($\Theta_D = 150°K$)[10] both short-wavelength acoustic phonons and optical phonons will be excited appreciably over most of the range of measurement,[11] and rough estimates show that their amplitudes are about 0.1 Å at 300°K. The corresponding time-averaged effect on the magnetic-dipole terms can readily be estimated using the known dependence of the α's on the pair separation ($\alpha = g^2\mu_B^2/r^3$). It is found that the effects are quite small compared with the observed temperature dependences, and we can conclude that the α's provide an accurate measure of the mean distances between the spins in individual pairs. Values of r obtained in this way for both the nn and nnn pairs are listed in Table I. As expected, they lie between the spacings in $LaCl_3$ and $GdCl_3$, and they vary approximately linearly with temperatures above 150°K.

For the exchange constants, however, the relative contributions of the thermal expansion and lattice vibrations to the observed temperature dependence are not so easy to estimate, since there is at present no satisfactory theory for the origin of the interactions. We may note, however, that the magnitudes of both J_{nn} and J_{nnn} decrease smoothly with increasing temperature, suggesting that thermal expansion is again more important than the lattice vibrations. If we make the ad hoc assumption that the vibration effects are in fact negligible, we can eliminate the temperature to find the exchange explicitly as a function of the pair separation. The results are shown in Fig. 2(b). Although both curves are quite smooth, it is not possible to fit them unambiguously to any specific functional form, since the ranges over which the r's vary are very limited. However, the results may be summarized in terms of the logarithmic derivatives:

$$x_{nn} = \frac{d(\ln J_{nn})}{d(\ln r_{nn})} = -13 \pm 4$$

and

$$x_{nnn} = \frac{d(\ln J_{nnn})}{d(\ln r_{nnn})} = -22 \pm 6.$$

The difference between these derivatives is striking, as is the very large value for x_{nnn}, although a value almost as large (-18 ± 6) has recently been reported for EuO.[12] The value for x_{nnn} is in clear contradiction with the recently proposed tenth-power law for superexchange.[13]

These experiments have shown that it is possible to obtain very precise values of exchange and dipolar interactions from the epr spectra of individual pairs when the two effects are comparable. The results for Gd^{3+} pairs in $LaCl_3$ prove that the nn exchange is relatively weak and antiferromagnetic, while the nnn exchange is four times stronger and ferromagnetic, removing the ambiguity in earlier speculations based on bulk measurements.[14] We have no fundamental explanation for these differences nor for the observed temperature dependences of the exchange constants, both of which seem to require an extension of the usual superexchange theory.

We wish to thank Dr. M. Blume, Dr. A. M. Clogston, Dr. J. Owen, Dr. R. G. Wheeler, and Dr. A. D. B. Woods for a number of helpful discussions.

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*This work supported in part by the U. S. Atomic Energy Commission.

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[1] See for example J. Owen, J. Appl. Phys. 32, 2135 (1961).

[2] M. T. Hutchings and W. P. Wolf, in Proceedings of the International Conference on Magnetism, Nottingham, England, 1964 (The Institute of Physics and the Physical Society, London, England, 1965), p. 342; J. M. Baker, Phys. Rev. 136, A1341 (1966).

[3] W. H. Zachariasen, J. Chem. Phys. 16, 254 (1948).

[4] Additional crystal field terms allowed by symmetry are found to be negligible.

[5] C. A. Hutchison and E. Wong, J. Chem. Phys. 29, 754 (1958).

[6] R. J. Birgenau, M. T. Hutchings, and W. P. Wolf, to be published.

[7] The difference between the two cases is believed to be due to the low symmetry about the nnn pair axis. This is discussed in detail in Ref. 6.

[8] The errors quoted in Table I represent the accuracy of changes in the parameters rather than their absolute values, which may be affected by small additional terms in the spin Hamiltonian, such as biquadratic exchange.

[9] L. Néel, J. Phys. Radium 12, 258 (1951); R. Aléonard and J. C. Barbier, Compt. Rend. 245, 831 (1957); R. Pauthenet and P. Blum, Compt. Rend. 239, 33 (1954).

[10] F. Varsanyi and J. P. Maita, Bull. Am. Phys. Soc. 10, 609 (1965).

[11] I. Richman, R. Satten, and E. Wong, J. Chem. Phys. 39, 1833 (1963), have shown that such modes lie as low as 50 cm^{-1} in LaCl$_3$.

[12] D. A. McWhan, P. C. Sauers, and G. Jura, Phys. Rev. 143, 385 (1966).

[13] D. Bloch, J. Phys. Chem. Solids 27, 881 (1966).

[14] E. L. Boyd and W. P. Wolf, J. Appl. Phys. 36, 1027 (1965).

ISOELECTRONIC DONORS AND ACCEPTORS

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(Received 29 June 1966)

It is reported that a hitherto unexplained optical transition in ZnTe is due to oxygen substituting isoelectronically for Te. A classification of isoelectronic traps into isoelectronic donors and acceptors is made. One striking difference between these two classes is apparent in the phonon sidebands of the $J=1$ and $J=2$ transitions occuring at each center.

The term isoelectronic trap[1] describes, in a semiconductor, a center which consists of an atom substituting isoelectronically for a host atom, and which will bind a hole and an electron to give a state in the forbidden band gap. Examples recognized so far by the radiative recombination of the bound hole and electron are N[1] or Bi[2] substituting for P in GaP, and Te[3] substituting for S in CdS. This paper reports another isoelectronic trap and shows that for all these traps a classification into isoelectronic donors and acceptors can be made.

In 1962, an extrinsic optical transition of unknown origin in ZnTe was reported[4] which fell 0.4 eV below the band gap. It was found to have two zero-phonon lines A and B ($J=1$ and $J=2$), which arose from the electron ($j=\frac{1}{2}$) and hole ($j=\frac{3}{2}$) coupling. Recently, crystals of ZnTe have been grown using SiO$_2$, BN, or carbon vessels to contain the molten salt. Runs identical in all respects, save that to one set 5 mole% ZnO was added to the melt, showed that the presence of oxygen increased the concentration of the center, as judged by its absorption spectrum, by at least a factor of 10. Before all measurements the crystals were quenched after equilibrating in 1 atm of Zn at 1000°C. The absence of fine structure in the A, B lines shows that it involves a simple point defect, and it is reasonable to conclude that this is oxygen substituting isoelectronically for tellurium.

Figure 1 shows an over-all view of the tran-

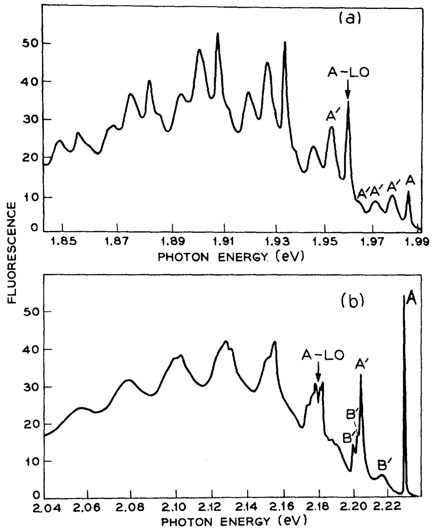

FIG. 1. (a) The fluorescent spectrum of oxygen, an isoelectronic acceptor, in ZnTe at 20°K. A is a zero-phonon line, lifetime broadened by decay of the $J=1$ state to the lower energy $J=2$ state.[4] Some of the phonon replicas of A are marked A'. The LO replica is also indicated. The zero-phonon line falls about 0.4 eV below the band-gap energy of ZnTe. (b) A similiar spectrum for the isoelectronic donor Bi in GaP. An analogous A line, and its phonon wings, is seen. In addition there are phonon wings of the B transition, B', as shown by the temperature variation of the spectrum and comparison with the low-temperature spectrum [Fig. 2(d)]. The zero-phonon line falls 0.1 eV below the band-gap energy of GaP. All spectra are taken using a photomultiplier with $S20$ response.