where $\mathcal{E}_k$ is an optical transition energy. These excitation energies correspond to the direct interband gaps $\mathcal{E}_k^0$ in the one-electron approximation but are lowered by the electron-hole interaction which shifts oscillator strength to lower photon energies. By combining Eqs. (A1)–(A3) one obtains

$$\Delta W = \langle \psi | H | \psi \rangle - \langle 0 | H_0 | 0 \rangle = -\lambda^2 E^2 \sum_k \mathcal{E}_k^{-1} . \quad \text{(A4)}$$

The susceptibility is defined as

$$\chi = \frac{\partial}{\partial E} \langle \psi | P | \psi \rangle = 2\lambda \sum_k f(k) , \quad \text{(A5)}$$

and using Eqs. (A3) and (A4)

$$\Delta W = -\lambda^2 E^2 \sum_k \mathcal{E}_k^{-1} = \tfrac{1}{2} \chi E^2 , \quad \text{(A6)}$$

which is the classical result obtained by using the variational principle instead of solving a boundary-value problem. The classical boundary-condition solution does not make clear the equivalence of transverse and longitudinal fields in the long-wavelength low-frequency limit with respect to the total energy of the solid.[15]

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Nuclear Quadrupole Resonance and Magnetic Relaxation in $(La\text{Gd})Al_2$ †

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Nuclear-quadrupole-resonance and relaxation measurements have been made at low temperatures in the dilute $(La\text{Gd})Al_2$ system at zero and low applied magnetic fields. The results complement those of McHenry, Silbernagel, and Wernick at high fields, and are consistent with the onset of magnetic order in the Gd random-spin system.

McHenry, Silbernagel, and Wernick[1-3] (hereafter referred to as MSW) have recently reported a series of nuclear-resonance and relaxation measurements in the pseudobinary alloy system $(L\alpha\text{Gd})Al_2$. Their results were consistent with the absence of long-range magnetic order in this system, even in alloys with up to 10 at.% Gd and at temperatures below 4.2 K. Magnetization measurements in the same system[4] indicated that, on the contrary, magnetic order is formed at or above 1.5 K for Gd concentrations above 2 at.%. Thus an apparent discrepancy exists between the nuclear-relaxation and magnetization results. MSW point out, however, that their relaxation measurements were carried out in applied magnetic fields of greater than 2.5 kOe, whereas the magnetization measurements were made for the most part in low fields, of the order of 250–500 Oe. MSW speculated that the ordering process might affect magnetization and high-field nuclear-relaxation measurements quite differently, and also that the field might itself strongly influence the magnetic order.

We wish to report the results of Al^{27} nuclear-quadrupole-resonance (NQR) and relaxation measurements on the $(La\text{Gd})Al_2$ system in zero and small applied fields which confirm qualitatively the first, and possibly the second, of the above speculations. The Al^{27} nuclei are situated in noncubic sites in the cubic Laves-phase $LaAl_2$ lattice,[5,6] and in zero static field exhibit the usual NQR spec-

trum of two lines for the Al^{27} spin $I=\frac{5}{2}$. The NQR resonance and relaxation results reported here are consistent with the establishment of magnetic order among the Gd spins at low temperatures for applied fields below 150 Oe, in contrast to the high-field results of MSW, and indicate that either the nature of the order itself, or the way in which the nuclei are affected by the ordering process, must change appreciably with field.

*La*Gd alloys containing 2, 5, and 10 at.% Gd were arc cast from 99.9%-pure constituents, turned, and remelted ten times to ensure homogeneity. Stoichiometric quantities of *La*Gd and 99.999%-pure Al metal were arc cast, turned, and remelted five times. Powered samples were prepared by crushing in an agate mortar and pestle and passing the comminuted material through a 90-μ sieve.

The $\frac{5}{2}$-$\frac{3}{2}$ quadrupole resonance was observed at a frequency of 1.485 ± 0.005 MHz at temperatures below 20 K. The corresponding quadrupole-coupling constant e^2qQ/h is 4.95 ± 0.02 MHz, which is about 7% larger than that reported by Jaccarino *et al.*[7] in pure $LaAl_2$. NQR measurements were also made on a sample of nominally pure $LaAl_2$.[8] No dependence of e^2qQ/h on Gd concentration was observed for less than 5 at.% Gd. (The signal from the 10-at.%-Gd sample was too weak to permit either accurate measurement of e^2qQ/h or spin-lattice-relaxation measurements.) Spin-echo NQR amplitude, linewidth, and relaxation measurements were made using a conventional transient NMR-NQR spectrometer.

Figure 1 gives the maximum spin-echo amplitude as a function of temperature in the 1.5–20-K range for the 2-, 5-, and 10-at.%-Gd samples. It is evident that although the 2-at.% sample exhibits a Curie-law temperature dependence for all but the lowest temperatures, the spin-echo amplitude for the 5- and 10-at.% samples drops markedly below the Curie-law value below a characteristic temperature which is an increasing function of Gd concentration. (Data for the nominally pure sample are not shown in Fig. 1; they follow a Curie-law dependence on temperature above the superconducting transition at 3.24 K.) Apart from a slight decrease of signal amplitude in applied field, attributable to Zeeman broadening of the quadrupole resonance, the amplitude results were essentially independent of static applied field less than 150 Oe.

NQR linewidth measurements were made by recording the spin-echo profile. The spin-echo inhomogeneous lifetime T_2^*, defined as the time required for the echo to decay to $1/e$ of its maximum amplitude, was thereby obtained. Spectrometer bandwidth limitations imposed a minimum resolution time of about 2 μsec on these measurements. The results are summarized in the empirical relation

$$1/T_2^* = A + Bx + CH_0 , \tag{1}$$

where x is the Gd concentration, H_0 the applied static field, $A=0.08\pm0.02$ μsec^{-1}, $B=0.008\pm0.003$ $(\mu sec\ at.\%)^{-1}$, and $C=0.009\pm0.005$ $(\mu sec\ Oe)^{-1}$. The most remarkable aspect of these results is the absence of any measurable dependence of T_2^* on temperature: The spin-echo amplitude decrease is not accompanied by an increase in linewidth as the temperature is lowered. Apparently nuclear spins are "lost" from the line in an all-or-nothing fashion.

Spin-lattice-relaxation measurements were made by monitoring the recovery to equilibrium of the spin-echo signal $V(t)$ as a function of elapsed time t after an initial saturating pulse. The data were fit to a recovery curve of the form

$$V(t) = V_0 + (V_1 - V_0) \sum_{i=1}^{I-1/2} a_i \exp\left[\frac{-b_i t}{T_1} - \left(\frac{b_i t}{\tau_1}\right)^{1/2}\right], \tag{2}$$

suggested by the high-field results of MSW and the "diffusionless" relaxation behavior observed by Tse and Hartmann using a different technique.[9] The coefficients a_i and b_i are known for the given initial conditions and the governing master equation,[10] and the parameters V_0, V_1, T_1, and τ_1 were varied for the best least-squares fit.

Figure 2 gives the dependence of T_1 and τ_1 on temperature for the 2- and 5-at.%-Gd samples. The results shown are for zero applied field, but no systematic variation of the relaxation with field was observed within the experimental error. The

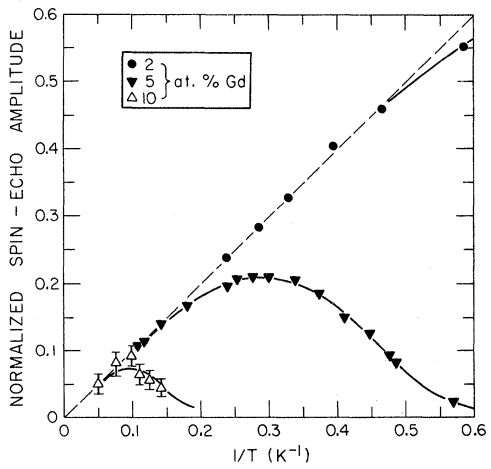

FIG. 1. Dependence of the normalized NQR spin-echo amplitude on reciprocal temperature and Gd concentration in the $(La\text{Gd})Al_2$ alloy system. The departure from Curie-law behavior is attributed to the onset of magnetic order in the Gd spin system. The data have been arbitrarily normalized to unity slope at high temperatures.

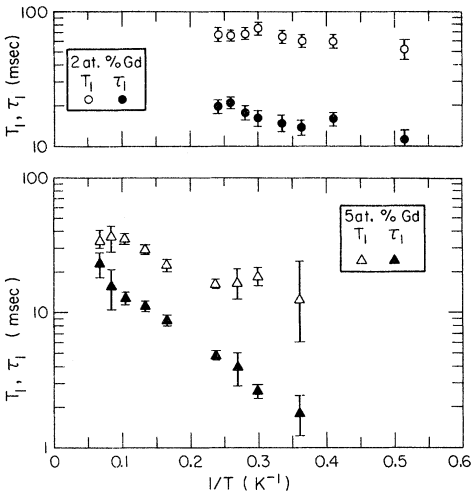

FIG. 2. Temperature dependence of the spin-lattice-relaxation times T_1 and τ_1, obtained as described in the text, for 2 and 5 at. % Gd in $LaAl_2$.

fits showed some systematic deviation of the experimental recovery function from the assumed form of Eq. (2), and the results given in Fig. 2 should not be taken as indicative of more than the qualitative behavior of the relaxation. Notable features of these results include (i) the sharp decrease of τ_1 with decreasing temperature in the 5-at.% sample, and (ii) the fact that the value of T_1 obtained by the fit procedure is one or two orders of magnitude faster than the Korringa relaxation time in pure $LaAl_2$.[1,2]

All of the above results can be understood in a model which attributes the resonance behavior to a progressive ordering of the Gd spin system as the temperature is decreased. Static alignment of the Gd spins in their mutual effective local fields inhomogeneously broadens the NQR line via the hyperfine interaction between Gd impurities and Al^{27} nuclei. The all-or-nothing manner in which this broadening takes place resembles the quadrupole broadening of the nuclear magnetic resonance by nonmagnetic impurities observed in Cu-based alloys by Bloembergen and Rowland.[11] Only those nuclei in essentially zero static hyperfine field contribute to the NQR line. The temperature at which the spin-echo amplitude begins to deviate from Curie-law behavior is given in Table I, as well as ferromagnetic Curie temperatures for nearby Gd concentrations as determined by Maple.[4] The numerical agreement is good, although probably fortuitously so.

The field dependence of the linewidth is adequately explained by Zeeman broadening of the NQR line, as the observed coefficient C in Eq. (1) is comparable to the Al^{27} nuclear gyromagnetic ratio. The fact that the observed concentration dependence of the linewidth does not itself depend on temperature makes it unlikely that magnetic interaction with the Gd spins is involved. The electric field gradient at the nuclei is probably more inhomogeneous in the presence of impurities than in the pure host.

The rapid decrease of the relaxation time τ_1 in the 5-at.% sample with decreasing temperature is to be contrasted with the opposite behavior in high fields reported by MSW. (The interpretation of τ_1 is more direct than that of T_1,[1] and we shall concentrate on the former.) The high-field results were attributed to a dependence of the Gd-spin-system polarization on temperature and field given by the appropriate Brillouin function, together with no dependence of the Gd spin-correlation time τ_m on field or temperature. This model always leads to an increase in relaxation time with decreasing temperature whatever the nature of the relaxation mechanism,[1-3,12] and thus cannot explain the present low-field NQR results.

The effect of the onset of magnetic order on nuclear relaxation has been treated only for the usual cases of materials in which the spins are arranged on a periodic lattice. Here two mechanisms can cause the relaxation time to decrease as the ordering temperature is approached from above. These are (a) enhancement of the fluctuating hyperfine field by the formation of ferromagnetic pair (and higher-order) correlations,[13] and (b) a critical-point singularity in τ_m, which decreases the nuclear relaxation time as long as τ_m^{-1} remains greater than the nuclear-resonance frequency.[14] No treatment of these mechanisms in dilute random magnetic alloys is known to the authors, although it is not unreasonable to suppose that their effects are qualitatively similar to those in the usual periodic lattice.

In zero field, T_1 is found to be appreciably shorter than the Korringa value. This result can be attributed to the effect of dipolar coupling between the nuclei, which tends to maintain the nuclear

TABLE I. Comparison of magnetic-ordering temperatures in the $(La\text{Gd})Al_2$ system as determined by zero-field NQR and low-field bulk-magnetization measurements.

Gd concentration (at.%)	θ_{nuc} (K)[a]	θ_c (K)[b]
2	1.5–2	•••
5	4–5	•••
10	10–20	•••
1.897	•••	1.5 ± 0.3
4.959	•••	4.0 ± 0.2
9.846	•••	10.0 ± 0.3

[a]Temperature at which the NQR spin-echo amplitude begins to deviate from a Curie-law temperature dependence.

[b]Ferromagnetic Curie temperature from Ref. 4.

spin system in internal thermal equilibrium via diffusion of spin energy.[2,15] MSW found no evidence for such dipolar effects at high fields, although the large quadrupolar splitting and inhomogeneous linewidth due to Gd polarization precluded an extensive investigation of this problem. The behavior of T_1 as discussed by MSW should in any case not be particularly sensitive to the exact value of T_1.[16] The observed NQR values of T_1 and τ_1 can be used to obtain an estimate of the effective dipolar coupling (or, equivalently, the spin-diffusion constant); the result is not too different from that obtained from the measured NQR spin-echo-envelope lifetime (phase memory time) $T_2 = 150 \pm 30$ μsec.

For the 5-at.%-Gd sample, T_1 decreases less quickly below than above 5 K, the temperature at which magnetic order first appears. This observation is consistent with the above model, since the static impurity polarization associated with the onset of order would be expected to partially quench the dipolar coupling.

Thus, the picture of a magnetically ordered impurity-spin system in low fields, obtained from magnetization measurements,[4] is confirmed by the present NQR results. On the other hand, the high-field relaxation behavior observed by MSW was accounted for by them in a model which assumed a *non*interacting impurity-spin system, even at temperatures well below the low-field Curie point. This is a remarkable state of affairs, since the applied field required for transition from low- to high-field behavior (~1 kOe) is only a small fraction of the average exchange field as obtained from the low-field Curie temperature.

A similar situation has been encountered in susceptibility measurements on other dilute magnetic alloys,[17,18] for which the large susceptibility found near the Curie point in zero field is markedly reduced in applied fields of a few hundred Oe. The latter results have received a theoretical treatment based on the oscillatory nature of the RKKY impurity-spin coupling and the presence of spatial inhomogeneity in the impurity-spin system.[19] Although this model has implications for the nuclear-relaxation results, the experimental and theoretical situations are far from settled.

MSW discuss an alternative explanation of their results which invokes the possibility that their high-field NMR experiments selectively sample only nuclei whose relaxation is essentially the same as in the noninteracting impurity-spin case. In this picture nuclei within an "observation radius" of ordered impurity spins or spin clusters are subjected to a strong static hyperfine field, which shifts them out of the resonance line. Only those nuclei are observed which lie in regions far from ordered impurity spins.

Unfortunately the present NQR results yield little further insight into the problem, other than that low-field magnetic order is observed by essentially the same method which yields no evidence of order at high field. Our observations seem to be compatible with the first model outlined above, but the second explanation also fits the available data: In zero field the observation radius may be considerably reduced by the absence of a field-induced impurity-spin polarization, and the zero-field experiments may sample nuclei which are strongly affected by the ordering process.

MSW point out the desirability of more magnetization data to help resolve the quandary. We would like to note that neutron-scattering experiments[18] could be expected to yield detailed information on the nature of the spin ordering.

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Electron-Phonon Resonance and Magneto-Optic Properties of Semiconductors*

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A many-body theory is developed for the influence of resonant electron-phonon coupling on the magneto-optic properties of semiconductors. In general, both self-energy effects and phonon-induced singularities in the electron-light coupling contribute to the light cross section. We examine the relative importance of the above contributions for three distinct cases and compare our results with previous theories.

Recently there has been considerable interest in the magneto-optic properties of semiconductors.[1] Conventional theoretical understanding of resonant structure in optical properties such as absorption,[2] photoconductivity,[3,4] and combined resonance[5] has been based on singularities in the electron propagator corresponding to the coupled electron-phonon systems (i.e., self-energy effects). Recently, however, an alternate approach based on phonon-induced resonant electron-light coupling, i.e., vertex effects[6] neglecting self-energy effects, has also been presented and invoked to explain anomalies in the photoconductivity data.[3] Because both theoretical approaches seem to be successful, it appears that self-energy effects (SE) and vertex corrections (VC) should be treated on an equal footing.

In this paper we present a systematic study of magneto-optic properties by distinguishing cases which are dominated by SE, VC, or both effects. Thus we attempt to synthesize previous theoretical work in an appropriate framework and point out their inadequacies in certain cases.

Our results and their connection to previous work can be understood physically from the schematic diagrams of Fig. 1. Previous theories[1-4,7] based on self-energy corrections include the renormalization of the electron propagator (heavy lines), as shown in Fig. 1(a). Our previous work[6] was based on resonances in the electron-light-interaction vertex considering the diagrams of Fig. 1(b) but neglecting self-energy effects; thus the electron propagators (light lines) were not renormalized by the coupling to the phonons represented by the dashed lines. As shown in Fig. 1(c), in the present work we consider both self-energy effects and the electron-light vertex terms; electron-phonon-vertex corrections have also been taken into account, but turn out to be small.[8]

The formal structure of our theory is apparent from Fig. 1(c), and consists of a geometric series whose terms could be singular. In the latter case the sum of the series gives a function whose poles are not the same as the singularities of the first term alone [i.e., Fig. 1(a)]. This feature is present in other systems such as the familiar random-phase-approximation (RPA) treatment of the electron gas.

The diagrammatic contributions of Fig. 1 can be expressed in simple physical terms by use of perturbation theory as well. Thus the electronic self-energy contribution involves the hybridization of a pure electronic state (say ϕ_e) with composite states consisting of an electron and a phonon. On the other hand, the vertex corrections involve the hybridization of the electron-hole pair (created by the incident light) with a phonon. It should be emphasized that the mechanism responsible for the hybridization in both cases is the *weak* electron-phonon interaction. Thus in both cases we expect significant hybridization only when the states involved are nearly degenerate. The near degeneracy (hereafter referred to as resonance) gives rise to the familiar level splitting into two branches, as