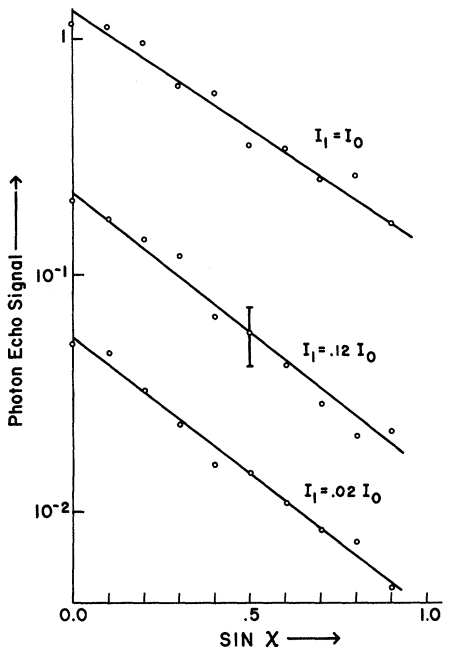

FIG. 2. Angular dependence results for several input intensities I_1, as calibrated by Fig. 1(a), where I_0 corresponds to an average θ_1 of the order of $\frac{1}{2}\pi$. Results from repeated runs show the slope to be independent of input intensity to within an uncertainty of ±15%.

that pulse-induced dephasing is not important here. The magnetic field effects are believed to be due to Cr^{3+}-Al interactions,[2,8] and the details remain to be calculated.

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NUCLEAR RELAXATION AND PAIR CORRELATION IN PARAMAGNETS

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From NMR relaxation studies, experimental and theoretical evidence is obtained for electron-spin pair-correlation effects in paramagnets.

Nuclear spin-lattice relaxation caused by indirect hyperfine coupling between paramagnetic spins and the nuclei of nonmagnetic ions has been studied in the paramagnetic state of magnetically ordered systems. These measurements were made at sufficiently high temperatures for critical fluctuation phenomena to be unimportant. Direct measurements of the spin-lattice relaxation time (T_1) were made on the Al^{27} nuclei in the XAl_2 (X = rare earth) intermetallic compounds using transient techniques. An unexpected but substantial temperature variation of T_1 of Al^{27} is observed at high temperatures. It is also noted that a large, and as yet unexplained, temperature variation of the F^{19} linewidth ($\Delta H \sim 1/T_2 \sim 1/T_1$) exists well above T_N in MnF_2. We will demonstrate that both the sign and magnitude of the temperature dependences are associated with

short-range electron-spin correlation in the paramagnetic state.

The T_1 measurements were made on fine powders (<400 mesh) of the XAl_2 compounds at temperatures from 77 to 373°K in an external magnetic field of 9 kOe using a phase-coherent, pulsed-nuclear-resonance spectrometer. All XAl_2 compounds except $PmAl_2$ were examined. No spin echo was observed in $EuAl_2$, $GdAl_2$, and $TbAl_2$, and, although the echo was observable in $DyAl_2$, $HoAl_2$, $ErAl_2$, and $TmAl_2$, the lines were too broad (~500 G for the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition) for the line to be saturated.[1] The linewidths were sufficiently narrow (<50 G for the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition) for T_1's to be measured in the magnetic $CeAl_2$, $PrAl_2$, $NdAl_2$, and $SmAl_2$ compounds and the nonmagnetic compounds $LaAl_2$, $YbAl_2$, and $LuAl_2$. A comb of 50-100 pulses with an rf field strength of 30-40 G was sufficient to saturate the resonance line. The recovery of the magnetization was exponential and T_1's measured in external fields of 9 and 6.3 kOe were equal to within experimental error.

In the nonmagnetic compounds of this series ($LaAl_2$, $YbAl_2$, $LuAl_2$) $1/T_1$ is proportional to T, as expected for nuclear relaxation via itinerant electrons. We find that $1/T_1T = 0.94$ and 0.107 (°K sec)$^{-1}$ for $LaAl_2$ and $LuAl_2$, respectively. Using the Korringa relation

$$\left[\frac{1}{T_1T} = \frac{4\pi k}{\hbar}\left(\frac{\gamma_n}{\gamma_e}\right)^2 K^2\right],$$

these values of $1/T_1T$ are in agreement with the previously determined values of the Knight shift ($K \simeq 0.075\%$).[1] The approximate equality of $1/T_1T$ in $LaAl_2$ and $LuAl_2$ indicates that the itinerant electron band structure is similar for all of the electronically isomorphic cubic Laves-phase compounds.[2]

The T_1's in the magnetic compounds are substantially faster and have a different temperature dependence. The data obtained for $CeAl_2$, $PrAl_2$, and $NdAl_2$ are summarized in Table I, and the data for $LaAl_2$ are also given for comparison. Two qualitative features are immediately obvious: (1) As the temperature is lowered, T_1 decreases in the paramagnetic compounds, and (2) the T_1's are shorter in compounds with higher Curie temperatures.

The behavior of T_1 in the paramagnetic state can be qualitatively explained by assuming the presence of two relaxation processes,

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)_s + \left(\frac{1}{T_1}\right)_f, \tag{1}$$

where $(1/T_1)_s$ is the ordinary itinerant-electron Korringa relaxation and $(1/T_1)_f$ is caused by the f-electron–nuclear interaction. Since $1/T_1$ for $LaAl_2$ and $LuAl_2$ is so similar, we assume that $(1/T_1)_s$ is the same for all XAl_2 compounds and equal to $1/T_1$ for $LaAl_2$. We therefore define

$$\left(\frac{1}{T_1}\right)_f^{\text{expt}} \equiv \left(\frac{1}{T_1}\right)^{\text{obs}} - \left(\frac{1}{T_1}\right)_{LaAl_2}.$$

This $(1/T_1)_f$ could result from either a direct dipolar interaction[3] or an indirect interaction via the conduction electrons, or both. However, the calculated dipolar relaxation rates are too small to account for $(1/T_1)_f^{\text{expt}}$ and are from one to two orders of magnitude smaller than that deduced for the indirect process. We describe the latter using an effective hyperfine Hamiltonian of the form $\mathcal{H} = A'\vec{I}\cdot\vec{S}$ compounded from an itinerant electron-f exchange interaction expressed as $\mathcal{H}_{ex} = \mathfrak{I}_{sf}\vec{S}\cdot\vec{s}$ and the normal itinerant-electron hyperfine interaction $\mathcal{H} = A\vec{I}\cdot\vec{s}$. Empirical values for A' are obtained from Knight-shift measurements. In the notation given here, $A' = (\gamma_n/\gamma_e) \times K_0\mathfrak{I}_{sf}$ and values for K_0 and $\mathfrak{I}_{sf}$ are given in Ref. 1. The relaxation rate can be expressed in terms of autocorrelation functions using the techniques of Kubo and Tomita,[4] and the result ob-

Table I. Spin-lattice relaxation rates in XAl_2 compounds. (Values of $1/T_1$ for the Al^{27} nuclei are given in units of sec^{-1}.)

T (°K)	$LaAl_2$	$CeAl_2$ $(1/T_1)^{\text{obs}}$	$CeAl_2$ $(1/T_1)_f^{\text{expt}}$	$PrAl_2$ $(1/T_1)^{\text{obs}}$	$PrAl_2$ $(1/T_1)_f^{\text{expt}}$	$NdAl_2$ $(1/T_1)^{\text{obs}}$	$NdAl_2$ $(1/T_1)_f^{\text{expt}}$
77	7.4	74	66	280	273	...	...
190	16.4	68.0	51.6	194	178.6	344	328
300	28.2	71.5	43.3	178	149.8	303	275
373	35.1	80	45	166	131	274	239
$(1/T_1)_f^{\text{theor}}$			61.5		124		182

tained in the infinite temperature limit is[5]

$$\left(\frac{1}{T_1}\right)_f^{\text{theor}} = \tfrac{1}{3}(2\pi)^{1/2}\left(\frac{A'}{\hbar}\right)^2 S(S+1)\tau_c, \qquad (2)$$

where it is assumed that the s-f exchange causes the f-electron spin autocorrelation function $\langle S_i(\tau)S_i(0)\rangle$ to decay with a characteristic time $\tau_c \simeq \hbar E_F/(\mathfrak{I}_{sf})^2 \simeq 10^{-14}$ sec.[6] Comparison of $(1/T_1)_f^{\text{expt}}$ and $(1/T_1)_f^{\text{theor}}$ in Table I indicates that this indirect mechanism is sufficient to account for the observed relaxation rate.

The calculations in Ref. 5 indicate that the temperature dependence of the relaxation rate should be extremely weak. In light of this, the substantial temperature dependence of the present observations is surprising. Further, previous measurements of the F^{19} NMR in paramagnetic MnF_2 showed that ΔH (which is related to T_1)[7] narrows significantly as the temperature is lowered.[8] Therefore, the observations indicate that spin-lattice relaxation in MnF_2 decreases as T is lowered, while it increases under the same conditions in the XAl_2 compounds.

A property common to both the Al^{27} site in XAl_2 and the F^{19} site in MnF_2 is that the hyperfine field at these sites is the result of indirect hyperfine interactions with the neighboring magnetic atoms. Fluctuations of the electronic spins on these atoms cause spin-lattice relaxation and the linewidth. At infinite temperature, these spins are completely uncorrelated and make statistically independent contributions to the components of the fluctuating hyperfine fields at the nucleus. However, with decreasing temperature the paramagnetic spins develop parallel (antiparallel) correlations in ferromagnets (antiferromagnets). In the limit that kT is high compared with any anisotropy or Zeeman energy, the hyperfine fields remain random, but with magnitudes which are correspondingly enhanced (reduced) in ferromagnets (antiferromagnets). This explains the fact that relaxation rates (or linewidths) increase in ferromagnets and decrease in antiferromagnets as the temperature decreases and pair correlation becomes increasingly important.

The case of the F^{19} nucleus in MnF_2 is shown explicitly in the insert to Fig. 1, where S_1, S_2, and S_3 contribute to the hyperfine field at the F^{19} site and spins S_1 and S_3 and S_2 and S_3 are coupled by antiferromagnetic exchange. As a result of the exchange coupling, pair correlation function

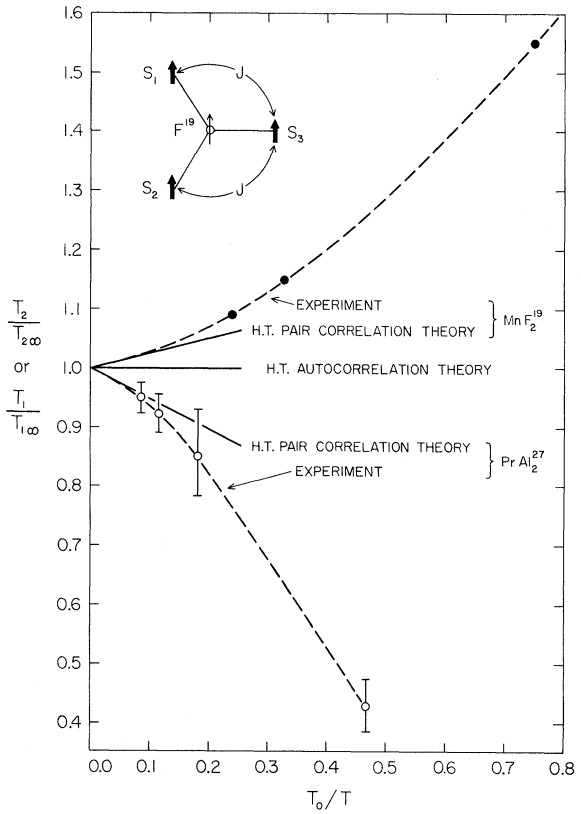

FIG. 1. Relaxation rates as a function of T_0/T for MnF_2[19] and $PrAl_2$[27]. Included for comparison are the results (to order J/kT) of the high-temperature pair-correlation theory discussed in this paper and the autocorrelation theory of Moriya (Ref. 3). The range of validity of the first-order pair-correlation theory is $T > 5T_0$. The local environment of the F^{19} nucleus in MnF_2 is shown in the insert.

for (S_1, S_3) and (S_2, S_3) will be nonvanishing and must be included along with the autocorrelation functions in any calculation of T_1 and ΔH. The temperature dependence resulting from such pair correlations is illustrated by the following model calculation. Neglecting the effect of an external magnetic field, and assuming an isotropic hyperfine interaction, the Hamitonian describing the system is of the form

$$\mathcal{H} = AI_z(S_{1z}+S_{2z}+S_{3z}) + \sum_{i<j} J_{ij}\vec{S}_i\cdot\vec{S}_j, \qquad (3)$$

where J is assumed to be much greater than A and limited to next-nearest neighbors. Using the equation of motion method, the second moment has the form

$$\hbar\langle\omega^2\rangle = A^2\{\langle S_{1z}S_{1z}\rangle + \langle S_{2z}S_{2z}\rangle + \langle S_{3z}S_{3z}\rangle + \langle S_{1z}S_{2z}\rangle + \langle S_{2z}S_{3z}\rangle + \langle S_{3z}S_{1z}\rangle\}, \qquad (4)$$

where

$$\langle S_{i\alpha}S_{j\beta}\rangle = \mathrm{Tr}\{S_{i\alpha}S_{j\beta}e^{-\beta_0\mathcal{H}}\}/\mathrm{Tr}\{e^{-\beta_0\mathcal{H}}\},$$

$$\beta_0 = 1/kT.$$

In the high-temperature limit $\langle S_{iz}S_{jz}\rangle = \frac{1}{3}S(S+1)\times\delta_{ij}$ and no pair correlation exists. Expanding $e^{-\beta_0\mathcal{H}}$ to first order in J/kT in the expression for the expectation value, the two nonvanishing terms are $\langle S_{1z}S_{3z}\rangle = \langle S_{2z}S_{3z}\rangle = -4(J/kT)[\frac{1}{3}S(S+1)]^2$, so a temperature-dependent pair correlation term exists. In the exchange-narrowed limit,[9]

$$\frac{1}{T_1}\simeq\frac{1}{T_2}=\gamma\Delta H\left(\frac{\gamma\pi}{2\sqrt{3}}\right)\frac{\langle\omega^2\rangle^{3/2}}{\langle\omega^4\rangle^{1/2}}.$$

A similar calculation of the fourth moment $\langle\omega^4\rangle$ shows its temperature dependence to be weak and to be equivalent to that of the autocorrelation function calculated by Moriya.[3] It is interesting to note that this temperature variation is much weaker than that of the pair correlation. Hence we ascribe the observed variation in T_1 and ΔH to the temperature dependence of the second moment. Relating T_C to J using the molecular-field approximation, we obtain,

$$\frac{1}{T_1}\simeq\frac{1}{T_2}\propto\left(1-\frac{1}{4}\frac{T_N}{T}\right). \tag{5a}$$

Employing a similar argument for the $X\mathrm{Al}_2$ compounds,

$$\frac{1}{T_1}\simeq\frac{1}{T_2}\propto\left(1+\frac{1}{2}\frac{T_c}{T}\right). \tag{5b}$$

The experimental data for T_1 for MnF_2[19] and $PrAl_2$[27] are shown in Fig. 1 as a function of T_0/T, where T_0 is the ordering temperature ($T_0 = T_N = 67°K$ for MnF_2; $T_0 = T_C = 35°K$ for $PrAl_2$). In addition, the temperature dependence predicted from Eqs. (5a) and (5b) are plotted. All of this is to be contrasted to the case of a nucleus coupled to only one spin, where $\langle\omega^2\rangle\propto\langle S_{iz}S_{iz}\rangle$ and as discussed above, the temperature dependence of T_1 or ΔH is expected to be negligible. As one example, a measurement of the Mn^{55} NMR linewidth in MnO in the paramagnetic state indeed shows $(\Delta H)^{55}$ to be temperature independent.[10]

In conclusion it has been shown that pair correlation accounts for the appropriate sign and magnitude of the temperature dependence of the observed relaxation processes in the case of indirect coupled hyperfine interactions. In these cases, relaxation measurements can serve as a useful tool for the determination of pair correlation. It is significant to note that deviations from the first-order high-temperature expansion occur at $T\sim 5T_C$, indicating a substantial amount of short-range order even at these temperatures. It should also be emphasized that the temperature dependence of the fourth moment, which is a measure of the autocorrelation function, is much weaker than that of the pair correlation. Therefore, the relaxation properties should show only a weak temperature dependence in the case of direct coupled hyperfine interactions. Preliminary measurements in $KMnF_3$ in the paramagnetic state also support these conclusions. Further work on these systems is in progress and will be reported elsewhere.

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[7]Kubo and Tomita demonstrate that, in the exchange-narrowed limit, the linewidth is directly related to the transverse and longitudinal correlation functions. Assuming that the fluctuations of the Mn spins and the hyperfine coupling are nearly isotropic in the paramagnetic state, we have the relation $\gamma\Delta H = 1/T_2 \simeq 1/T_1$.

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