THE $AuGa_2$ DILEMMA

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We report on measurements of the unusual temperature dependence of the Knight shift, nuclear spin-lattice relaxation, and susceptibility of $AuGa_2$. A phenomenological scheme is proposed which relates the three properties in terms of a changing atomic character to the wave functions of the itinerant electrons at the Fermi surface.

Among the myriad of nonmagnetic metals, alloys, and intermetallic compounds that have been studied, only a few show an appreciable temperature dependence to their Knight shifts. Of these few solids $AuGa_2$ alone has a Knight shift[1] which changes sign as a function of temperature (see Fig. 1). This is made all the more surprising by the following two facts: First, the isostructural (CaF_2-type), isoelectronic $AuAl_2$ and $AuIn_2$ intermetallic compounds have temperature-independent Knight shifts. Second, electronic specific heat[2] and de Haas–van Alphen (dHvA) Fermi surface[3] studies of the three metals give no indication of differences which pointedly would distinguish any one from the other or, for that matter, from what would reasonably be expected from a free-electron-like model.

In this note we report on a more detailed investigation of the magnetic properties of the $AuAl_2$, $AuGa_2$, and $AuIn_2$ metals including Knight shifts (K), nuclear spin-lattice relaxation rate ($1/T_1$), and static susceptibility (χ) measurements. We propose a phenomenological scheme which self-consistently relates the anomalous temperature dependencies to K, $1/T_1$, and χ in $AuGa_2$ in terms of a changing atomic character to the wave functions of the electrons at the Fermi surface as the temperature is increased.

NMR measurements. – The unusual behavior of the Ga^{71} Knight shift in $AuGa_2$ is shown in Fig. 1. By way of contrast the Al^{27} and In^{115} resonances in $AuAl_2$ and $AuIn_2$ have very nearly temperature-independent Knight shifts of $K^{27} = (0.056 \pm 0.005)\%$ and $K^{115} = (0.94 \pm 0.02)\%$, respectively, in the 4-300°K region. The results of the nuclear spin-lattice relaxation studies for the Al^{27} and Ga^{71} resonances in $AuAl_2$ and $AuGa_2$ are given in Table I. The quantity T_1T as well as T_1 is tabulated as a function of T because ordinarily one expects T_1T to be independent of T, regardless of the origin of the nuclear spin–itinerant electron scattering process (orbital, dipolar, contact spin, or core polarization).[4] Indeed this is seen to be precisely the case for the Al^{27} NMR in $AuAl_2$, as it is for nearly all metals. Again, a very few solid metals exhibit a weak (<20%) temperature dependence to T_1T, but only in $AuGa_2$ has a variation of T_1T by more than a factor of 5 been found.

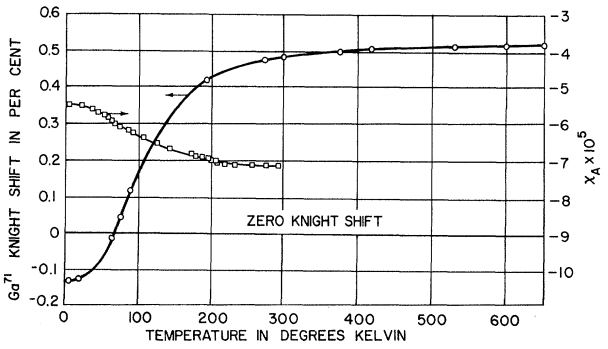

FIG. 1. The Ga^{71} Knight shift versus temperature in $AuGa_2$. The measurements were extended to 650°K to see if the Knight shift began to decrease again. This would be expected on a two-narrow-band model, one empty, one filled symmetrically, positioned with respect to E_F (see Reference 6). Also shown is the magnetic susceptibility versus temperature of $AuGa_2$. A large part of the temperature-independent diamagnetism must be attributed to the Au- and Ga-ion cores. The remaining part probably arises from intra- or interband contributions [see K. Yamaji and R. Kubo, J. Phys. Soc. Japan 25, 330 (1968)].

Table I. Nuclear spin-lattice relaxation time T_1 of the Al^{27} NMR in $AuAl_2$ and Ga^{71} NMR in $AuGa_2$. The infinite temperature value of T_1T for $AuGa_2$ was obtained via graphical extrapolation and is used in the plot of $D'(T)$ in Fig. 2. If one uses the measured value of T_1T in $AuAl_2$ and the Knight shift and T_1T of Al^{27} in aluminum metal, $K^{27}=0.161\%$ and $T_1T=1.72$ sec °K, respectively, and assumes in both metals that the shift and T_1 arise from s electrons alone, one obtains from the Korringa relation ($1/T_1T \propto K^2$) a predicted value of $K^{27}(AuAl_2)$ of 0.050 %, to be compared with the observed value of 0.056 %. If we use the appropriate Korringa-like relations for orbital and core-polarization interactions, for p electrons we would predict a value of $T_1T \simeq 1$ sec °K at 4.2°K, and for s electrons at $T=295$°K, a value of $T_1T=0.11$ sec °K.

NMR	T (°K)	T_1 (msec)	T_1T (°K sec)
Al^{27} in $AuAl_2$	4.2	4400	18.5
	20	•••	•••
	77	250	19
	195	•••	•••
	295	62	18.3
	∞[a]	•••	(18.6)
Ga^{71} in $AuGa_2$	4.2	158	0.665
	20	31.5	0.630
	77	3.42	0.263
	195	0.67	0.13
	295	0.41	0.12
	∞[a]		(0.111)

[a]Extrapolated

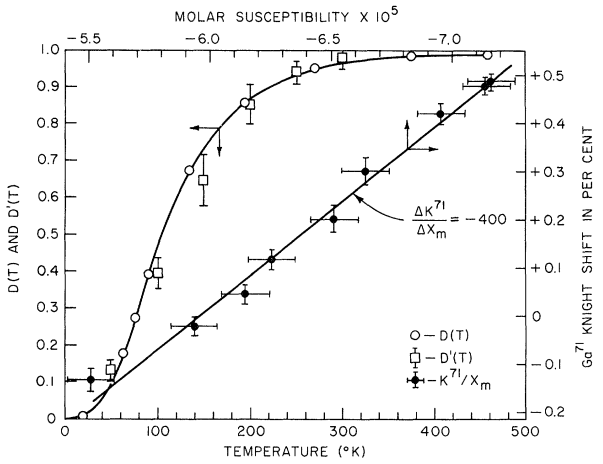

FIG. 2. The Ga^{71} Knight shift versus the molar susceptibility in $AuGa_2$ with temperature being the implicit parameter. The error bars are estimated uncertainties in the combined measurements at particular temperatures. Also shown are the quantities $D(T) \equiv [K(T)-K(0)]/[K(\infty)-K(0)]$ and $D'(T) \equiv [R(T)-R(0)]/[R(\infty)-R(0)]$ versus temperature for the Ga^{71} NMR in $AuGa_2$.

χ measurements. – No less significant is the difference in the variation of the magnetic susceptibility with temperature in the three metals. While all are diamagnetic – as are many of the nontransition metals – it is only in $AuGa_2$ that an appreciable temperature dependence to χ is manifest (see Fig. 1). At first sight the variation of χ with T in $AuGa_2$ appears to be proportionately less dramatic than are the corresponding variations of K and T_1T. However, much of the diamagnetism is intrinsic to the ion cores and is temperature independent as is clearly shown by the temperature-independent susceptibilities of $AuAl_2$ ($\chi=-3.54\times10^{-5}$/g atom) and $AuIn_2$ ($\chi=11.75\times10^{-5}$/g atom).

Interpretation. – One might begin by attempting to correlate the various anomalies in the magnetic properties of $AuGa_2$. As has proven useful a number of times in studies[5] of certain of the transition metals, we plot $K^{71}(T)$ vs $\chi(T)$ with temperature being the implicit parameter. This is shown in Fig. 2. Within the uncertainties of both experiments, the plot yields a linear relation with slope $\Delta K^{71}/\Delta\chi=-400$ (emu/mole)$^{-1}$. Although we may draw some comfort from this simple proportionality, the large negative value of $\Delta K^{71}/\Delta\chi$ is quite puzzling. In previous studies,[5] when $\Delta K/\Delta\chi$ was found to be negative it was immediately interpreted in terms of a spin–core-polarization hyperfine field. However, as we shall see, the value of $\Delta K^{71}/\Delta\chi=-400$ is at least an order of magnitude larger than could reasonably be attributed to core-polarization effects, the only mechanism presumably responsible for negative hyperfine fields.

How then do we interpret a Knight shift that becomes increasingly positive with temperature as the susceptibility, to which it is proportional, becomes increasingly negative? Two features of the Knight shift are suggestive as to the manner in which to proceed. Below 65°K, $K^{71}<0$ indicating p core-polarization effects predominate at low temperatures. On the other hand, at elevated temperatures K^{71} is large and positive indicating the s contact interaction now is dominant. Hence without making resort to any physical model we take recognition of the fact that the majority carrier wave functions are p-like at low temperature and become completely s-like at higher temperatures in the following manner. As regards the Ga^{71} Knight shift, we arbitrarily assume it to be of form

$$K(T)=K_p[1-D(T)]+K_sD(T), \qquad (1)$$

where $D(T)$ is a monotonically increasing function of T defined by the relation $D(T)=[K(T)-K(0)]/[K(\infty)-K(0)]$; hence $0 \leq D(T) \leq 1$ for all T. With $K_p \equiv K(0) = -0.133\%$ and $K_s \equiv K(\infty) = +0.51\%$ the particular temperature dependence of $D(T)$ is shown in Fig. 2.

Likewise the same assumption of a $p \rightarrow s$ "metamorphosis" would suggest the relaxation rate to be given by

$$R(T) \equiv \frac{1}{T_1(T)T} = \left(\frac{1}{T_1 T}\right)_p [1-D'(T)] + \left(\frac{1}{T_1 T}\right)_s D'(T) \quad (2)$$

with $D'(T)$ defined in analogous fashion to $D(T)$. Noting that $(1/T_1T)_p \equiv R(0) = 1.5(\text{sec } ^\circ\text{K})^{-1}$, and, by extrapolation of the available data, that $(1/T_1T)_s \equiv R(\infty) = 9.0$ (sec °K)$^{-1}$, we find the values of $D'(T)$ shown in Fig. 2. (The actual points are taken from a best-fit plot of $1/T_1T$ vs T.) The quantities $D(T)$ and $[1-D(T)]$ as defined above are simply the probabilities for the electrons at the Fermi surface to be of either s or p symmetry at temperature T, respectively. Thus we would expect $D(T) \equiv D'(T)$ and experiment confirms this conjecture. The importance of this will be assessed below.

Before we may relate Knight shift with susceptibility we must know, or otherwise obtain, the appropriate hyperfine coupling constant. Optical hfs studies yield a value of $H_{4s} = 1.0 \times 10^7$ Oe for the hyperfine field per 4s electron spin. We obtain the core-polarization field H_{4p} as follows: From the low-temperature electronic specific heat[2] $\gamma = 6.45 \times 10^{-4}$ cal/mole deg^2 we compute a low-temperature Pauli paramagnetic susceptibility $\chi = 3.7 \times 10^{-5}$ emu/mole. (This neglects possible electron-electron enhancement of χ and electron-phonon enhancement of γ.) Then using a tight binding model for the Knight shift in an intermetallic compound[5] we find for the Ga resonance in $AuGa_2$

$$K(0) = CH_{4p}(\tfrac{1}{2}\chi)\eta_{Ga}{}^p \quad (3)$$

with $C = 0.895 \times 10^{-4}$ cgs units. Choosing $\eta_{Ga}{}^p \simeq 1$ and noting $K^{71}(0) = -0.133\%$, we find $H_{4p} \simeq (1/10) \times H_{4s}$. This is similar to the ratio of s contact to d core-polarization fields found necessary to interpret the Knight shifts and susceptibilities of the transition metals. We are now in a position to generalize Eq. (3) so as to use it with Eq. (1) to determine $\chi_p(T)$ and $\chi_s(T)$; namely

$$K_p(T) = \tfrac{1}{2}CH_{4p}\chi_p(T)\eta_{Ga}{}^p;$$

$$K_s(T) = \tfrac{1}{2}CH_{4s}\chi_s(T)\eta_{Ga}{}^s. \quad (4)$$

From Eqs. (4) and (1) we obtain the following expression for K and χ:

$$K(T) = K(0)[1-4.9D(T)],$$

$$\chi(T) = \chi_{dia} + \zeta\chi_p(0)[1-0.61D(T)], \quad (5)$$

where we have taken $\eta_{Ga}{}^s = \eta_{Ga}{}^p = 1$ and lumped all of the temperature-independent diamagnetism in χ_{dia}. The factor ζ reflects the Landau-Peierls diamagnetism of the majority carriers which we assume to be proportionately temperature dependent. Taking $\zeta = \frac{2}{3}$, corresponding to $m^*/m = 1$, we may now evaluate $\Delta K/\Delta\chi$. The calculated and experimental values are

$$\left(\frac{\Delta K}{\Delta\chi}\right)_{calc} = -420(\text{emu/mole})^{-1};$$

$$\left(\frac{\Delta K}{\Delta\chi}\right)_{exp} = -400(\text{emu/mole})^{-1}.$$

Considering the approximations involved the agreement is most satisfying. Thus the initially puzzling result of a large negative $(\Delta K/\Delta\chi)_{exp}$ is seen to be a manifestation of a decreasing paramagnetism accompanying the change in character of the wave functions of the itinerant electrons at the Fermi surface.

As additional support for the "all $p \rightarrow$ all s" hypothesis we note that the observed relaxation rates at the two extremes of the temperature scale are reasonably consistent with the p (core polarization plus orbital) and s (contact) hyperfine interactions, respectively, using Korringa-like ($1/T_1T \propto K^2$) relations. (See caption Table I.) Concerning the temperature-independent values of the Knight shifts in $AuAl_2$ and $AuIn_2$ and the relaxation rate in $AuAl_2$, we find that they are what one would predict from predominantly s-character itinerant electrons at all temperatures.

Clearly some unusual discontinuities to the band structure of $AuGa_2$ must exist very near the Fermi surface. However no rigid-band–model calculations that we have attempted will reproduce the behavior of $D(T)$.[6] What appears to be required is a temperature-dependent lattice potential that allows the Fermi surface to "warp"

in such a manner as to satisfy the changing symmetry character of the electrons at the extremes of temperature and, at the same time, approximately conserve their total number at $E = E_F$. The phenomenology proposed in this note in no way resolves the dilemma of why the dHvA Fermi surface studies show no large differences to the energy surfaces in $\vec{k}$ space for the three metals. It is our belief that were it possible to do dHvA, cyclotron-resonance, etc., experiments at somewhat higher temperatures (~50-100°K), noticeable differences might become apparent in the electron dynamics. Strong evidence already exists for this contention insofar as the temperature dependence of the thermoelectric power of $AuGa_2$ differs markedly from that of the other two metals.[7]

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$E2$ CORE POLARIZATION BY THE $h_{9/2}$ PROTON

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The half-life of the 8^+ state of ^{210}Po has been measured. An effective charge of $(1.68 \pm 0.09)e$ (including proton charge) for the $h_{9/2}$ proton orbit has been deduced from the analysis of the three experimental $B(E2)$ values with use of the radial integral for a Saxon-Woods potential.

As reported in a recent paper of Yamazaki and Ewan,[1] the nanosecond time analysis of γ rays in the reaction ^{208}Pb$(\alpha, 2n)^{210}$Po revealed a new isomeric state of about 150-nsec half-life which was assigned to the expected 8^+ member of the $(h_{9/2})^2$ configuration (see Fig. 1). Since those states, as shown in Fig. 1, are practically of unique $(h_{9/2})^2$ configuration from the shell-model point of view,[2] each $B(E2)$, after being divided by the corresponding statistical factor S, should yield an effective charge common to all the $E2$ transitions within the band. Yamazaki[3] made such a discussion of the $E2$ effective charge derived from this half-life as well as already known half-lives[4] of the 4^+ and 6^+ members, but a small discrepancy among $B(E2)/S$ values was observed. It might be ascribed to an uncertainty in the previous experi-

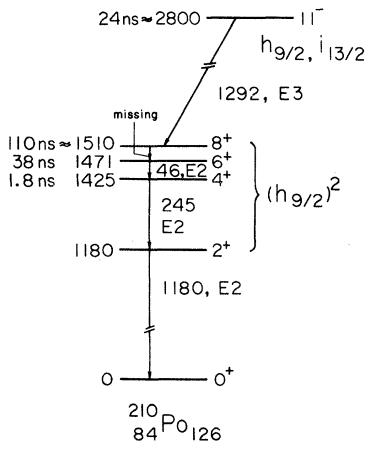

FIG. 1. Level scheme of ^{210}Po established by Yamazaki and Ewan (Ref. 1). The new half-life is entered.