PHYSICAL REVIEW B VOLUME 7, NUMBER 4 15 FEBRUARY 1973

Nuclear Magnetic Resonance, Magnetic Susceptibility, and Lattice Constants of Solid and Liquid $AuGa_2$, $Au_{0.95}Pd_{0.05}Ga_2$, and $AuIn_2$

W. W. Warren Jr., R. W. Shaw Jr.,* A. Menth,† F. J. DiSalvo, A. R. Storm, and J. H. Wernick
Bell Laboratories, Murray Hill, New Jersey 07974

(Received 6 June 1972)

We report measurements of the magnetic susceptibility, Knight shift, and nuclear spin-lattice relaxation rates in the pure compounds $AuGa_2$ and $AuIn_2$ and an alloy of nominal composition $Au_{0.95}Pd_{0.05}Ga_2$. Measurements were made in both the solid and liquid states over a temperature range from 4.2 to 1100 K. Lattice constants were measured from 4.2 to 300 K for $AuAl_2$, $AuIn_2$, and $Au_{0.95}Pd_{0.05}Ga_2$ and to 715 K for $AuGa_2$. The susceptibilities, Ga Knight shifts, and magnetic relaxation rates of $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$ exhibit complex temperature dependences which, with the exception of the Knight shift, continue to the vicinity of the melting point. The Knight shifts become constant above 400 K. At low temperatures the Knight shifts and relaxation rates in $Au_{0.95}Pd_{0.05}Ga_2$ are strongly enhanced relative to $AuGa_2$, but the alloy data converge to those of the pure compound as the temperature increases. The changes in magnetic properties at the melting point are small compared with their temperature-dependent variations in the solid state. Lattice-constant data for $AuGa_2$ and $AuIn_2$ suggest anomalous thermal-expansion behavior for these compounds below 100 K. The magnetic properties of $AuIn_2$ exhibit comparatively weak temperature dependence over the entire temperature range covered. We propose a phenomenological explanation for these results in terms of temperature-dependent modification of the electronic structure toward an essentially free-electron situation in the solid near the melting point.

I. INTRODUCTION

The fluorite-structure intermetallic compounds AuX_2 (X = Al, Ga, or In) have recently received considerable attention, in part because of the so-called "$AuGa_2$ dilemma."[1] In $AuGa_2$, the Ga Knight shift ($\mathcal{K}^{69,71}$) is strongly temperature dependent and ranges from a modest negative value at 4.2 K to a large, positive, and temperature-independent value above 400 K. The magnetic susceptibility (χ) and the nuclear spin-lattice relaxation rate ($1/T_1$) have also been found to exhibit unusual temperature dependences below 300 K.[1] This behavior of the magnetic properties of $AuGa_2$ contrasts sharply with that of the corresponding quantities in $AuAl_2$ and $AuIn_2$. In the latter metals and, in fact, in virtually all other nonmagnetic metals, $\mathcal{K}$ is positive and $\mathcal{K}$, χ, and $(T_1T)^{-1}$ are nearly constant over wide ranges of temperature.[1,2] Historically, the unique behavior of the magnetic properties of $AuGa_2$ was difficult to reconcile with the results of specific-heat measurements,[3] Fermi-surface studies,[4,5] and transport measurements.[6] With the exception of the thermoelectric power, these properties are qualitatively similar for the three AuX_2 compounds.

Recent theoretical and experimental advances have provided important new information about the electronic structure of $AuGa_2$ at low temperatures. Switendick and Narath[7] performed augmented-plane-wave (APW) band-structure calculations that show an unusually flat band ($\Gamma_{2'}$-X_3), which, they suggest, lies just below the Fermi level in $AuGa_2$. This band is derived mainly from Ga-Ga s-like antibonding states, whereas the states on the Fermi surface have mainly Ga-p and Au-s character. The absence of s character at the Ga site would leave only a smaller, negative p-electron contribution to $\mathcal{K}^{69,71}$, while the presence of Au-s character leads to a large positive Au Knight shift ($\mathcal{K}^{197}$) at 4.2 K. In contrast, the $\Gamma_{2'}$-X_3 s band in $AuIn_2$ and $AuAl_2$ is only partially full and this results in larger, positive X-site shifts in these two metals. Carter, Weisman, Bennett, and Watson[8] have recently pointed out that the progressively lower calculated position of the s band in the order $AuAl_2$-$AuIn_2$-$AuGa_2$ is a reflection of the size of the atomic s-p splitting which increases in the order Al-In-Ga. The band-structure results are therefore consistent with an earlier deduction by Jaccarino, Weger, Wernick, and Menth,[1] who concluded from NMR and susceptibility data alone that Ga-s states are absent from the Fermi surface of $AuGa_2$ at low temperatures.

Several additional pieces of evidence add further support to the "missing-s-band" model. First, it has been found[2] that substitution of a few at.% Pd for Au in $AuGa_2$ results in sharply increased low-temperature magnetic susceptibility, superconducting transition temperature, and electronic heat capacity. Within the context of a rigid-band picture, substitution of Pd should lower the Fermi level, and thus these results suggest a sharply increasing density of states just below the Fermi level of pure $AuGa_2$. Second, de Haas–van Alphen studies by Jan *et al.*[4] and, more recently, by Longo *et al.*[9] have shown that the second-zone hole surface corresponding to the Ga-s band is absent in $AuGa_2$ at 4.2 K, whereas this surface is observed in $AuAl_2$ and $AuIn_2$. Finally, the most compelling evidence for the missing s-band model comes from the recent hydrostatic pressure experiments performed by Schirber[10,11] and by Weaver *et al.*[12] Measurements of the superconducting transition temperature[10] and de Haas–van Alphen frequencies[11] suggest that at a pressure of about 6 kbar a new piece (presumably the second-zone hole surface) is added to the Fermi surface. That these states are, in fact, of Ga-s character is clear from the pressure dependence of $\mathcal{K}^{69,71}$, which jumps abruptly to a large, positive value near 6 kbar.[12] Thus, the low-temperature electronic structure of the AuX_2 compounds and, in particular, the unique properties of $AuGa_2$ appear to be qualitatively explained within the framework of the band calculations.

The origin of the temperature dependence of the magnetic properties of $AuGa_2$ is, however, less clearly understood. Jaccarino *et al.*[1] proposed a phenomenological model in which the states at the Fermi surface convert from Ga-p to Ga-s character as the temperature is raised. The band calculations of Switendick and Narath[7] showed that an increase in Ga-s character would occur if the states at the top of the Ga-s band become depopulated at higher temperatures. They suggested that this might occur either through upward movement of the s band caused by thermal expansion or simple thermal generation of holes in a nearly rigid s band. Subsequent work by Schirber and Switendick[13] showed that the volume dependence of the s-band position has the wrong sign to allow the first mechanism. Furthermore, the hydrostatic pressure experiments indicate that the sharp band edge is sufficiently close to the Fermi level to permit appreciable thermal depopulation of the band. However, an additional mechanism that may also be important is modification of the band structure itself by thermal vibrations of the lattice. The role of this effect, operating in conjunction with thermal electronic excitations, will be considered in detail in this paper. Still one more puzzle, seemingly inexplicable on any existing model, is the observed *diamagnetic* variation of χ between 4.2 and 300 K.[1]

With the exception of $\mathcal{K}^{71}$ measurements in $AuGa_2$ which extend to 650 K,[1] previous work on the magnetic properties of the AuX_2 compounds has been limited to temperatures at or below room temperature. In the hope of obtaining improved understanding of the temperature-dependent effects in $AuGa_2$, we undertook an extension of measurements of χ, $\mathcal{K}$, and T_1 to the melting point (T_m) and into the liquid state. In particular, we wished to determine whether, as suggested by the work of Jaccarino *et al.*, the transition in the character of the states on the Fermi surface is completed when the temperature has reached 300–400 K. Furthermore, since the temperature-dependent effects seem to be consequences of some remarkably sharp features of the band structure, it was of interest to investigate possible changes in this structure at very high temperatures and when long-range order is destroyed by melting.

In this paper we describe measurements of χ, $\mathcal{K}$, and the magnetic contribution (R_M) to $1/T_1$ for Ga^{69} and Ga^{71} in $AuGa_2$ and in an alloy of nominal composition $Au_{0.95}Pd_{0.05}Ga_2$. The contributions of electric quadrupolar spin-lattice relaxation processes have been discussed in a previous paper.[14] As a standard for comparison with $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$, we have made similar measurements for In^{115} in solid and liquid $AuIn_2$. The NMR data extend from 4.2 to 1100 K, while the susceptibility measurements cover a range from 4.2 to roughly 30 K above T_m. Finally, in order to check for possible anomalous structural effects, the lattice constant was measured by x-ray diffraction from 4.2 to 300 K for $Au_{0.95}Pd_{0.05}Ga_2$, $AuIn_2$, and $AuAl_2$ and to 715 K for $AuGa_2$.

II. EXPERIMENTAL DETAILS

The sample materials used for these experiments were prepared by inductive melting of stoichiometric proportions of the appropriate elements (99.999+% purity) and they were purified by zone melting (two passes) in quartz ampoules. Additional details of the preparation and characterization of these materials have been presented previously.[2] The composition of our (nominally) $Au_{0.95}Pd_{0.05}Ga_2$ sample was checked by atomic absorption analysis which indicated an actual Pd concentration of 4.5 ± 0.2 at.%. The superconducting transition of our sample occurred over the range 1.62–1.77 K, in agreement with the transition temperature previously reported[2] for a sample containing 5 at.% Pd.

Samples used for susceptibility measurements consisted of single crystals whose dimensions were, approximately, 10×2×3 mm. For measurements above room temperature, the samples were sealed under an argon atmosphere in quartz ampoules. Powdered samples for NMR and x-ray studies were prepared by crushing and sieving the single-crystal material to obtain 325-mesh particles. For the high-temperature NMR measurements, sample powders were mixed with powdered quartz in roughly equal proportions. This procedure prevented sintering of the solid powders at high temperatures and provided a medium for dispersion of the liquid droplets above T_m. The powder mixtures were sealed under vacuum in quartz ampoules. For measurements at or below room temperature, NMR samples were unsealed and contained no quartz powder.

Magnetic susceptibilities were measured by the Faraday method in a field of approximately 13 kOe. For each sample the susceptibility was measured at several field values at room temperature in order to verify that the observed magnetization was linear in magnetic field.

NMR data were obtained with a coherent pulsed NMR spectrometer operating at a frequency of 16.0 MHz. Knight shifts for Ga^{69} and Ga^{71} were measured with respect to a reference sample of dilute aqueous solution of $GaCl_3$. In discussing the data, we shall refer only to the average value $\mathcal{K}^{69,71}$ of the measured shifts for the two isotopes. The reference sample for In^{115} was dilute aqueous solution of $In_2(SO_4)_3$.

Spin-lattice relaxation times were usually measured using approximately π-$\frac{1}{2}\pi$ rf pulse sequences and measuring the free-induction-decay amplitude with a boxcar integrator.[15] For low-temperature measurements care was taken to ensure that rf heating by the pulses was negligible. This was accomplished by verifying that the observed T_1 values were independent of the total power input to the samples. The measured values of $1/T_1$ for Ga^{69} and Ga^{71} were decomposed into separate contributions from magnetic and quadrupolar interactions using the method of isotopic decomposition.[16,17]

In the case of $Au_{0.95}Pd_{0.05}Ga_2$, the resonance line exhibited severe inhomogeneous broadening at low temperatures. In this case spin echoes were used to obtain measurements of $\mathcal{K}^{69,71}$ and T_1 and a saturating "comb" of pulses was used in place of a single π pulse when measuring T_1. The rotating rf field amplitude was about 100 Oe for these measurements.

The temperature dependences of the lattice constants were obtained with a General Electric type SPG x-ray diffractometer using Cu $K\alpha$ radiation. For each sample the absolute values of the diffractometer data were adjusted to agree with precise room-temperature values obtained with a 114.6-mm Debye–Scherrer camera. This procedure corrected for systematic errors in lattice constant resulting from small misalignments of the sample holder in the diffractometer. The largest correction of this type amounted to 0.015 Å for $Au_{0.95}Pd_{0.05}Ga_2$. The lattice constants were determined from the observed spectra by extrapolation of the positions of the high-angle lines according to the method of Nelson, Riley, Taylor, and Sinclair.[18]

III. EXPERIMENTAL RESULTS

Characteristic values are given in Table I for the susceptibility, Knight shift, total relaxation rates for Ga^{69} and Ga^{71}, and magnetic contributions for Ga^{71} in $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$. A similar tabulation of χ, $\mathcal{K}^{115}$, and $1/T_1$ data for In^{115} in $AuIn_2$ appears in Table II. In this section we summarize the most noteworthy features of these data, devoting particular attention to the temperature dependences of the various quantities measured.

A. Magnetic Susceptibility

Experimental values of the molar susceptibility χ_m are plotted in Fig. 1 for $AuGa_2$, $Au_{0.95}Pd_{0.05}Ga_2$,

TABLE I. Characteristic values of the molar susceptibility, $Ga^{69,71}$ Knight shift, Ga^{69} and Ga^{71} total relaxation rates, and Ga^{71} magnetic relaxation rate in pure $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$.

T (K)	χ (10^{-5} emu mol^{-1})	$\mathcal{K}^{69,71}$ (%)	R^{69}/T (sec K)$^{-1}$	R^{71}/T (sec K)$^{-1}$	R_M^{71}/T (sec K)$^{-1}$
		$AuGa_2$			
4.2	−5.50	−0.133[a]	...	...	1.50[a]
20	−5.53	−0.125[a]	...	...	1.55[a]
78	−6.05	+0.045 ± 0.003	2.05 ± 0.07	3.45 ± 0.15	3.45 ± 0.15
195	−6.98	0.415[a]	...	...	7.70 ± 0.4[a]
300	−7.15	0.480 ± .003	5.70 ± 0.20	8.60 ± 0.25	8.60 ± 0.25
400	−7.16	0.500 ± .003	5.30 ± 0.15	8.70 ± 0.25	8.7 ± 0.3
600	−6.75	0.505 ± .003	4.80 ± 0.20	7.10 ± 0.30	6.9 ± 0.4
765 (−)	−5.10	0.505 ± .003	4.65 ± 0.25	6.80 ± 0.35	6.5 ± 0.4
765 (+)	−3.10	0.484 ± .003	5.25 ± 0.20	6.20 ± 0.20	5.5 ± 0.3
1100	...	0.484 ± .003	3.80 ± 0.18	5.25 ± 0.25	5.0 ± 0.3
		$Au_{0.95}Pd_{0.05}Ga_2$			
4.2	−3.76	0.800 ± 0.100	12.5 ± 1.5	18.5 ± 2.0	18.5 ± 2.0
78	−4.23	0.635 ± 0.050	10.0 ± 1.5	16.0 ± 2.0	14.3 ± 1.5
195	−5.18	0.480 ± 0.015	6.0 ± 0.5	11.0 ± 0.6	11.0 ± 0.6
300	−5.94	0.505 ± 0.003	7.5 ± 0.4	10.7 ± 0.3	10.2 ± 0.6
400	−6.15	0.510 ± 0.003	6.4 ± 0.3	8.9 ± 0.3	8.5 ± 0.6
600	−6.55	0.509 ± 0.003	6.25 ± 0.25	7.9 ± 0.3	7.2 ± 0.5
765 (−)	−6.55	0.505 ± 0.003	6.10 ± 0.30	7.9 ± 0.4	7.2 ± 0.5
765 (+)	−3.10	0.480 ± 0.003	5.25 ± 0.25	7.05 ± 0.35	6.6 ± 0.4
1100	...	0.473 ± 0.003	4.25 ± 0.25	6.00 ± 0.30	6.3 ± 0.4

[a] Reference 1.

TABLE II. Characteristic values of the molar susceptibility, In^{115} Knight shift, and total relaxation rate in $AuIn_2$.

T (K)	χ (10^{-5} emu mol^{-1})	$\mathcal{K}^{115}$ (%)	$(T_1T)^{-1}$ (secK)$^{-1}$
4.2	−9.80	0.853 ± 0.003	11.00 ± 0.42
78	−9.80	0.871 ± 0.003	10.95 ± 0.45
300	−9.50	0.886 ± 0.003	11.40 ± 0.30
500	−9.12	0.892 ± 0.003	11.45 ± 0.30
700	−8.65	0.892 ± 0.003	12.05 ± 0.30
817 (−)	−8.35	0.897 ± 0.003	13.10 ± 0.30
817 (+)	−5.08	0.890 ± 0.003	19.45 ± 0.45
1100	...	0.875 ± 0.003	14.45 ± 0.45

and $AuIn_2$. All materials are diamagnetic over the entire temperature range covered.

In addition to the previously observed[1,2] increase in diamagnetism of $AuGa_2$ between 4.2 and 300 K, this material exhibits a striking variation in the *paramagnetic* direction between 550 K and T_m. A further and quite sluggish paramagnetic change was observed when $AuGa_2$ melted. With introduction of 5 at.% Pd, three main effects occur: (i) The diamagnetic susceptibility at 4.2 K is reduced by roughly 30%; (ii) the high-temperature paramagnetic variation is suppressed; and (iii) the melting-point transition becomes appreciably sharper for the same heating rate. The value of χ_m in the liquid is insensitive to 5-at.%-Pd doping.

The data for $AuIn_2$ exhibit a surprisingly large and nearly linear paramagnetic variation of χ_m between 200 K and T_m. Below 200 K, χ_m is essentially constant except for a small impurity "Curie tail" at very low temperatures. At the melting point, χ_m shifts in the paramagnetic direction, as in the case of the other two materials. A small sharp peak in χ_m was observed just above T_m. This effect and a similar effect observed on cooling are discussed in more detail in Sec. III E.

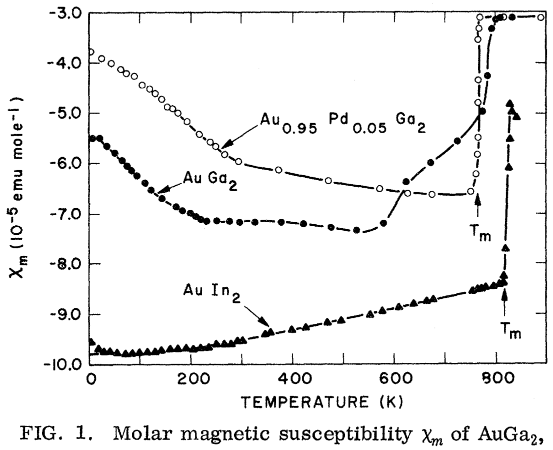

FIG. 1. Molar magnetic susceptibility χ_m of $AuGa_2$, $Au_{0.95}Pd_{0.05}Ga_2$, and $AuIn_2$ as functions of temperature. Data for $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$ below 300 K are from Ref. 2.

The absolute value of χ_m at 300 K observed for $AuIn_2$ in these experiments is roughly 20% smaller than that reported previously[2] by Wernick *et al.* Although the source of this discrepancy is not completely clear, it appears that error in calibration of the magnetic field gradient in the earlier work is the most likely cause.

B. Knight Shifts

The Knight shifts for Ga^{69} and Ga^{71} in $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$ and for Au^{197} in $AuGa_2$ are shown in Fig. 2. The $\mathcal{K}^{69,71}$ data in $AuGa_2$ are characterized by a smooth rise from a modest negative shift (−0.133%) at 4.2 K to a large, positive temperature-independent value (0.505%) above 400 K. The value of $\mathcal{K}^{69,71}$ decreases by 4% on melting and the shift above T_m is independent of temperature. In the range of their overlap, the present data are in good agreement with those of Jaccarino *et al.*[1] The Au^{197} shift measured by Switendick and Narath exhibits a *decrease* of 10 to 20% over the range in which $\mathcal{K}^{69,71}$ is increasing most rapidly.

The value of $\mathcal{K}^{69,71}$ in $Au_{0.95}Pd_{0.05}Ga_2$ is positive and the value at 4.2 K (0.800 ± 0.100%) exceeds the high-temperature value in $AuGa_2$. As the temperature is raised, the value of $\mathcal{K}^{69,71}$ in the alloy decreases to approach that of pure $AuGa_2$. This converging trend is emphasized by the shallow minimum in $\mathcal{K}^{69,71}$ observed near 200 K. Above 600 K, the values of $\mathcal{K}^{69,71}$ are essentially the same for $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$. The large error estimates for the shifts in the alloy at low temperatures result from increasing inhomogeneous broadening of the resonance lines as the sample

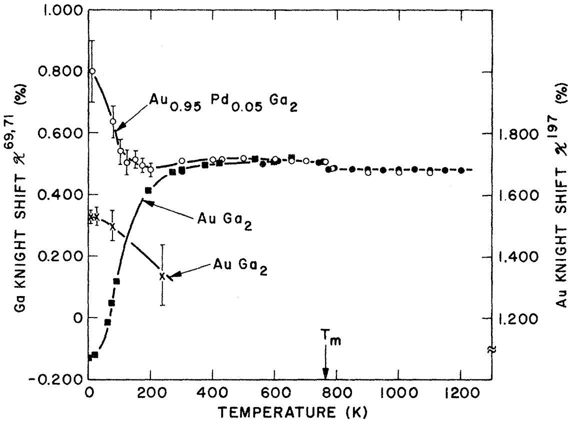

FIG. 2. Ga Knight shift $\mathcal{K}^{69,71}$ as a function of temperature in $AuGa_2$ (closed points) and $Au_{0.95}Pd_{0.05}Ga_2$ (open points) and Au Knight shift $\mathcal{K}^{197}$ (crosses) in $AuGa_2$. The $\mathcal{K}^{69,71}$ data in solid $AuGa_2$, denoted by closed squares, are from Ref. 1. The $\mathcal{K}^{197}$ data are from Ref. 7.

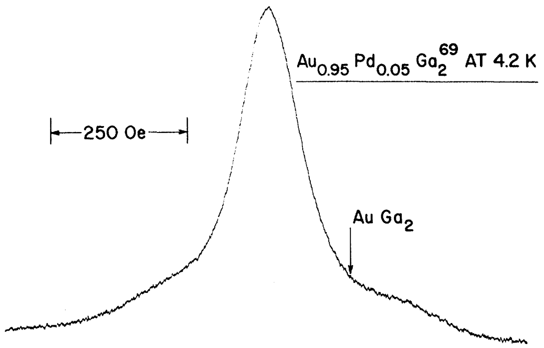

FIG. 3. Ga^{69} spin-echo intensity vs applied field for $Au_{0.95}Pd_{0.05}Ga_2$ at 4.2 K. The arrow indicates the resonance position for Ga^{69} in pure $AuGa_2$.

was cooled below 300 K. A spin-echo profile showing the distribution of local magnetic fields is reproduced in Fig. 3. The full width at half-maximum is 177 ± 2 Oe for Ga^{71} at 4.2 K and the linewidth was found to be proportional to the applied field.

Knight-shift data $\mathcal{K}^{115}$ for In^{115} in $AuIn_2$ are plotted in Fig. 4. The temperature dependence of $\mathcal{K}^{115}$ is very weak in comparison with $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$. The slight increase observed between 4.2 K and T_m is typical of simple metals. The value of $\mathcal{K}^{115}$ decreases by less than 1% at T_m.

C. Magnetic Spin-Lattice Relaxation Rates

Ga^{71} magnetic spin-lattice relaxation rates R_M^{71} for $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$ are given in Fig. 5 in the form R_M^{71}/T. The corresponding rates for Ga^{69} are smaller by a factor $(\gamma_{69}/\gamma_{71})^2$, where γ is the appropriate nuclear gyromagnetic ratio. The dominant features of the $AuGa_2$ data are a strong increase in R_M^{71}/T over the range in which $\mathcal{K}^{69,71}$ increases and a rather sharp drop occurring between 450 and 600 K. The latter effect, amounting to an approximately 30% decrease in R_M^{71}/T, occurs over a temperature range in which there is less than a 1% change in $\mathcal{K}^{69,71}$. The values of R_M^{71}/T for $Au_{0.95}Pd_{0.05}Ga_2$ are roughly an order of magnitude greater than for $AuGa_2$ at 4.2 K. As the temperature is increased, the $Au_{0.95}Pd_{0.05}Ga_2$ data converge to values of R_M^{71}/T slightly higher than those obtained for $AuGa_2$ at high temperatures.

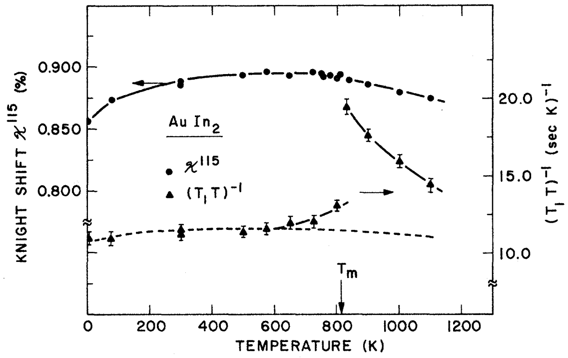

FIG. 4. In^{115} Knight shift $\mathcal{K}^{115}$ (circles) and total rerelaxation rate/temperature $(T_1T)^{-1}$ (triangles) as functions of temperature in $AuIn_2$. The broken line indicates an extrapolation of the magnetic relaxation rate based on $\mathcal{K}^2T_1T$ = const.

Experimental values of $(T_1T)^{-1}$ for In^{115} in $AuIn_2$ are shown in Fig. 4. These data for the *total* spin-lattice relaxation rate contain contributions from electric quadrupolar interactions that cannot be separated unambiguously by the isotopic decomposition method employed for the Ga isotopes. The data show $(T_1T)^{-1}$ to be constant below 600 K. Above this temperature, $(T_1T)^{-1}$ increases with temperature in the solid, jumps to a still higher value just above T_m, then drops rapidly as the liquid is heated above T_m. Since quadrupolar relaxation is generally associated with high-temperature ionic motions[19] (phonons and diffusion), it is reasonable to assume that the increased values of $(T_1T)^{-1}$ in the liquid and solid at high temperature result from quadrupolar processes.[14] An approximate decomposition is suggested in Fig. 4 in which the magnetic contribution at high temperatures is determined by extrapolation of the low-temperature data assuming $\mathcal{K}^2T/R_M$ to remain constant.

D. Lattice Constants

Lattice constants are plotted as functions of temperature in Fig. 6 for $AuGa_2$, $Au_{0.95}Pd_{0.05}Ga_2$, $AuIn_2$, and $AuAl_2$. Our observed values at 4.2 and

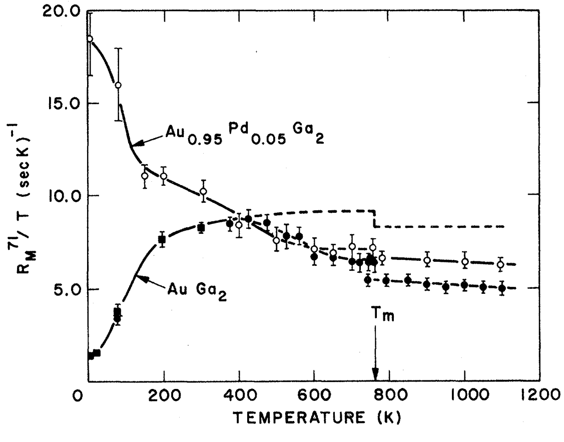

FIG. 5. Ga^{71} magnetic relaxation rate/temperature R_M^{71}/T as a function of temperature for $AuGa_2$ (closed points) and $Au_{0.95}Pd_{0.05}Ga_2$ (open points). The data in solid $AuGa_2$, denoted by closed squares, are from Ref. 1. The broken line indicates an extrapolation of the magnetic relaxation rate based on $\mathcal{K}^2R_M^{71}/T$ = const.

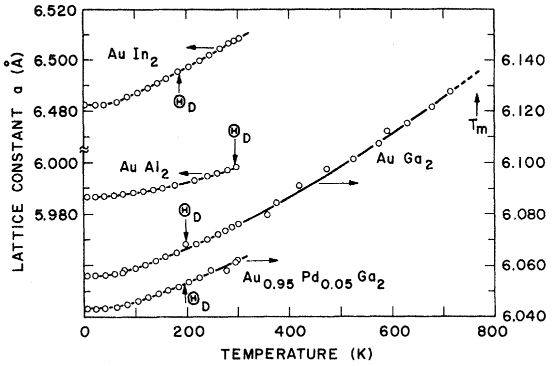

FIG. 6. Lattice constant a as a function of temperature for $AuAl_2$, $AuGa_2$, $AuIn_2$, and $Au_{0.95}Pd_{0.05}Ga_2$. The values of the Debye temperatures Θ_D are as given in Ref. 2.

300 K (Table III) agree well with those given by Jan *et al.*[4] and, with the exception of $AuIn_2$, with the older room-temperature values given by Pearson.[20] For $Au_{0.95}Pd_{0.05}Ga_2$ the room-temperature value is considerably smaller (0.008 Å) than reported in Ref. 2 for this composition. We believe the present value to be the more reliable, primarily because of our use of Cu radiation as compared with the Cr radiation used previously. The use of Cu radiation permits reading of more high-angle reflections and results in improved accuracy. This is particularly important for an alloy such as $Au_{0.95}Pd_{0.05}Ga_2$ in which the lines are severely broadened by strains and inhomogeneities.

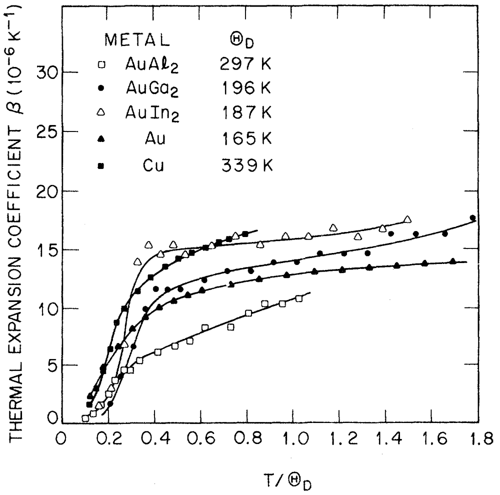

FIG. 7. Linear coefficient of thermal expansion β obtained from temperature dependence of the lattice constants of $AuAl_2$, $AuGa_2$, and $AuIn_2$ and plotted as a function of the reduced temperature T/Θ_D. Also shown, for comparison, are data for pure Au (Ref. 21) and pure Cu (Ref. 22).

The coefficient of linear thermal expansion $\beta \equiv (1/a)(\partial a/\partial T)_p$ was computed from smooth curves drawn through the data points for the pure compounds. These results are shown in Fig. 7 plotted against the reduced temperature T/Θ_D ($\Theta_D \equiv$ Debye temperature) for the three compounds and compared with published data for the pure fcc metals Au[21] and Cu.[22] The most striking thing about these results is the slower onset of thermal expansion and sharper knee in the curves for $AuIn_2$ and $AuGa_2$ compared with the behavior of Au and Cu. As may be seen in Fig. 6, the slow onset of thermal expansion also occurs for $Au_{0.95}Pd_{0.05}Ga_2$, although these lattice-constant data are less accurate than those of the pure materials. $AuAl_2$, on the other hand, behaves much more like Au and Cu if one takes into account its apparently smaller high-temperature value of β. The high-temperature lattice-constant data for $AuGa_2$ show that β continues to increase monotonically with temperature and reaches a value of $(24.0\pm1.0)\times10^{-6}\ K^{-1}$ at 700 K.

TABLE III. Lattice-constant values at 4.2 and 296 K for $AuAl_2$, $AuGa_2$, $Au_{0.95}Pd_{0.05}Ga_2$, and $AuIn_2$.

T (K)	$AuAl_2$	$AuGa_2$	$Au_{0.95}Pd_{0.05}Ga_2$	$AuIn_2$
4.2	5.9869 ±0.0020	6.0560 ±0.0020	6.0432±0.0040	6.4825±0.0020
296	5.9982 ±0.0010	6.0758 ±0.0010	6.0615±0.0030	6.5075±0.0020

E. Melting-Point Effects ($AuIn_2$)

The Knight shift and susceptibility of $AuIn_2$ exhibited unusual behavior in the vicinity of T_m. These data are shown in Fig. 8. In considering these data it is important to bear in mind that the

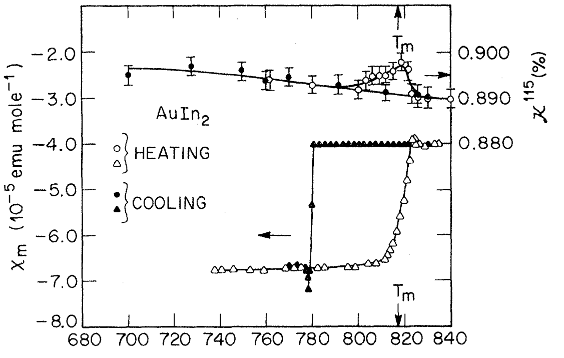

FIG. 8. Molar magnetic susceptibility χ_m and In^{115} Knight shift $\mathcal{K}^{115}$ in solid and liquid $AuIn_2$ near the melting point. Open points refer to data taken on heating while closed points were taken on cooling.

NMR samples were dispersed powders whereas the χ_m samples consisted of single pieces of $\mathrm{AuIn_2}$ crystal. Also, the measurements of $\mathcal{K}^{115}$ were made at a series of discrete temperature intervals and the samples were allowed to reach thermal equilibrium before measurements were made. The measurements of χ_m, on the other hand, were made with the temperature varying continuously at a rate of about 1.2 K/min. The width of the melting transition in the χ_m data is determined partially by latent-heat effects associated with the heating rate, while the width of the transition in $\mathcal{K}^{115}$ is due mainly to the thermal gradient across the sample.

The most interesting feature of the χ_m data is the small peak or overshoot following the paramagnetic change on metling and a corresponding effect on solidification following supercooling. The freezing effect on χ_m occurred about 40 K below T_m and was very abrupt. The $\mathcal{K}^{115}$ data also show a peak in the vicinity of T_m on heating. In the NMR samples freezing from the supercooled state occurred gradually over a relatively wide temperature range. The observed peaks in $\mathcal{K}$ and χ_m were unique to $\mathrm{AuIn_2}$ and were not observed for $\mathrm{AuGa_2}$ or $\mathrm{Au_{.95}Pd_{0.05}Ga_2}$.

IV. DISCUSSION

With the addition of the new data reported in Sec. III, there now exists a rather complete experimental description of the magnetic properties of the $\mathrm{Au}X_2$ compounds. $\mathrm{AuGa_2}$, the most "anomalous" of the three, has in particular been exhaustively studied. Yet to date there exists no detailed theoretical argument that can unify and explain the experimentally observed temperature-dependent magnetic properties of these materials.

Our own efforts to understand the $\mathrm{AuGa_2}$ dilemma have led us to consider a variety of theoretical mechanisms and to test these mechanisms against all the data available to us. While we are still not able to offer a comprehensive microscopic model for $\mathrm{AuGa_2}$, we have gradually established what we believe to be a consistent semiquantitative understanding of the problem. The purpose of this section is to present for the reader's consideration the outlines of our model, including the gaps that still remain.

A. Review of Magnetic Properties

We begin our discussion by reviewing very briefly the potentially important contributions to χ, $\mathcal{K}$, and R_M. This discussion will serve as a framework for our consideration of the properties of the $\mathrm{Au}X_2$ materials.

The susceptibility can be decomposed into ionic and electronic contributions

$$\chi = \chi_i + \chi_e , \tag{1}$$

where χ_i is the diamagnetic susceptibility of the Au- and the X-ion cores and χ_e is the total conduction-electron susceptibility. The electronic contribution can in turn be split into a paramagnetic (Pauli) part χ_e^p and a diamagnetic (Landau–Peierls) part χ_e^d, and for noninteracting free electrons these contributions have the form

$$\chi_e = \chi_e^p + \chi_e^d = 2\mu_B^2 N(E_F)\,[1 - \tfrac{1}{3}(m_0/m^*)^2]\Omega_m , \tag{2}$$

where μ_B is the Bohr magneton, $N(E_F)$ is the density of states at the Fermi level (per unit volume for single spin direction), m^*/m_0 is the effective mass ratio, and Ω_m is the molar volume. In general, electron-electron effects lead to enhancements of the paramagnetic term by a factor $(1-\alpha)^{-1}$, where the Stoner enhancement parameter α usually lies in the range $0.1 \leq \alpha \leq 0.5$.[23]

The Knight shift will, for the purposes of this paper, be considered to result from two contributions:

$$\mathcal{K} = \mathcal{K}_s + \mathcal{K}_p , \tag{3}$$

where $\mathcal{K}_s$ and $\mathcal{K}_p$ refer, respectively, to contributions from electrons having s and p character at the site of the resonant nucleus. The s-electron term results from the contact interaction and may be written

$$\mathcal{K}_s = \tfrac{8}{3}\pi \langle |\Psi(0)|^2 \rangle_F \chi_{e,s}^p , \tag{4}$$

where $\langle |\Psi(0)|^2 \rangle_F$ is the electron probability amplitude at the resonant nucleus averaged over all s electrons on the Fermi surface and $\chi_{e,s}^p$ is the paramagnetic spin susceptibility per atom of electrons having s character at the resonant nucleus. The local susceptibility $\chi_{e,s}^p$ represents one contribution to the total electronic paramagnetic susceptibility χ_e^p.

The p-electron shift $\mathcal{K}_p$ may result from a number of contributions including p-core-polarization,[24] short-range orbital (Van Vleck),[24,25] and long-range orbital (diamagnetic) terms.[26,27] The diamagnetic term is negative, the Van Vleck term is positive, and the core-polarization contributions may have either sign. In simple metals these terms are usually at least an order of magnitude smaller than the s-electron term. However, Watson *et al.*[27] have pointed out the possible dominance of the diamagnetic term in metals such as Bi having large diamagnetic susceptibilities ($m^*/m_0 \ll 1$).

The spin-lattice relaxation rate will be decomposed into three terms:

$$T_1^{-1} = R_Q + R_{M,s} + R_{M,p} , \tag{5}$$

where R_Q is the contribution from electric quadrupolar interactions and $R_{M,s}$ and $R_{M,p}$ are, respectively, the magnetic contributions from s- and p-like conduction electrons. The quadrupolar contribution is related mainly to the ionic dynamics in the solid at high temperatures and in the liquid. The R_Q data are discussed in detail in Ref. 14.

The s-electron magnetic relaxation rate is normally related to the corresponding Knight shift contribution $\mathcal{K}_s$ by the modified Korringa relation[28]:

$$R_{M,s} = 4\pi\gamma_n^2 kT\mathcal{K}_s^2 K(\alpha)/\gamma_e^2\hbar, \tag{6}$$

where $K(\alpha)$ is a correction factor for electron-electron effects. In simple metals $K(\alpha)$ usually lies in the range 0.5–0.7.[29,30]

The correction $K(\alpha)$ to the Korringa relation is a consequence of the q dependence of the dynamic susceptibility.[31] For a simple free-electron gas, the susceptibility per atom may be written[23]

$$\chi(q,\omega) = \frac{\chi^0(q,\omega)}{1 - 2V(q)\chi^0(q,\omega)/\hbar^2\gamma_e^2}, \tag{7}$$

where $V(q)$ is the q-dependent electron-electron interaction and $\chi^0(q,\omega)$ is the unenhanced susceptibility. The Knight shift is proportional to $\chi(0,0)$ and therefore is enhanced by the factor $(1-\alpha)$, where

$$\alpha = 2V(0)\chi^0(0,0)/\hbar^2\gamma_e^2 = V(0)N(E_F). \tag{8}$$

The relaxation rate, on the other hand, is related to $\chi(q,\omega_0)$, where ω_0 is the Larmor frequency, and since $\chi(q,\omega_0)$ decreases when $q \to 2k_F$,[32] the enhancement is reduced at high q.

The contributions to the magnetic spin-lattice relaxation rate from p electrons are usually much less important than their corresponding contributions to $\mathcal{K}$. For example, if $\mathcal{K}_p$ is due primarily to p-electron-core-polarization effects, the corresponding relaxation rate is proportional to $\mathcal{K}_p^2$ through a Korringa relation[33]

$$R_{M,p} = 4\pi\gamma_n^2 kT\mathcal{K}_p^2 K(\alpha)/3\gamma_e^2\hbar, \tag{9}$$

where the factor of 3 in the denominator results from the threefold orbital degeneracy of the p states. Because of the relatively small values of $\mathcal{K}_p$ compared to $\mathcal{K}_s$, $R_{M,p}$ may be expected to be negligible for core polarization, except in cases in which the conduction electrons are *predominantly* p-like. Similar arguments apply to the other possible p-electron contributions.[34]

B. Temperature Dependence of Magnetic Properties of $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$

It is convenient to partition the problem as illustrated in Fig. 9. We shall focus primarily on the magnetic properties of pure $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$, but we shall of course relate our discussion to the measured electronic properties of these materials and to the magnetic and electronic properties of $AuAl_2$ and $AuIn_2$ where that is appropriate. We have distinguished two temperature ranges in Fig. 9 and for each of these ranges we have indicated schematically the behavior of $\mathcal{K}^{69,71}$, R_M^{71}/T, and the total susceptibility χ_m. The results for $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$ are contrasted to illustrate the effect of Pd doping. In addition it is useful to consider separately the values of these properties in the limiting cases $T = 0$ and $T \simeq T_m$. These data may be found in Table I. This separation of the problem by temperature range may at first seem artificial. However, we believe that the behavior of the magnetic properties in each range can be discussed independently and we shall endeavor to justify the assumption as the discussion proceeds.

1. Properties at T = 0

There is now quite general agreement as to the qualitative features of the electronic structure of $AuGa_2$ at very low temperatures. The band-structure calculations made by Switendick and Narath indicate that $AuGa_2$ has a full Ga-s antibonding band with a sharp upper edge just below the Fermi level. That the band edge is indeed very close to E_F is evidenced by the hydrostatic pressure experiments performed by Schirber.[10,11] He found an abrupt change in the pressure dependence of one of the de Haas–van Alphen frequencies at a pressure of about 6 kbar. He has also observed a jump in the superconducting transition temperature at the same pressure. Both of these observations suggest that a new band with a high density of states reaches the Fermi level at this pressure, while the Knight-shift measurements of Weaver *et al.*[12] show that it has the required Ga-s character. From calculations of the dependence of the Ga-s band on lattice constant,[13] Schirber

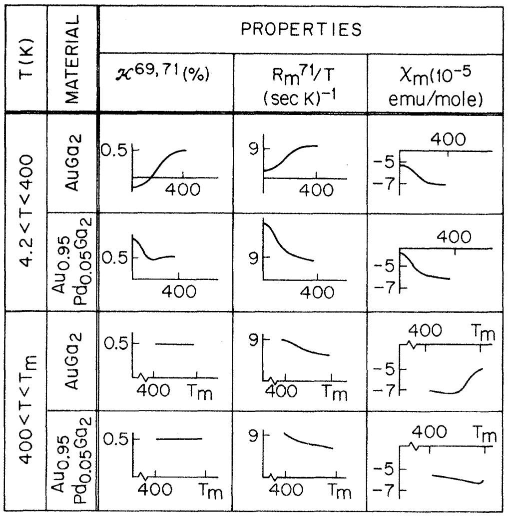

FIG. 9. Schematic presentation of the important features of the magnetic properties of $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$ in the temperature ranges $4.2 < T < 400$ K and 400 K $< T < T_m$.

estimates that the normal-volume s-band edge is on the order of only 0.010 eV below E_F. The remaining states at E_F are of primarily Ga-p and Au-s character, and these states give rise to the large positive value of $\mathcal{K}^{197}$ and the negative value of $\mathcal{K}^{69,71}$ at low temperatures. The similarity of the values of $\mathcal{K}^{197}$ observed in pure Au(1.64%)[35] and in $AuGa_2$(1.52%)[7] indicates that the Au-s density is not altered drastically in forming the intermetallic compound.

Although the negative value of $\mathcal{K}^{69,71}$ almost certainly results from p-electron effects, it is not possible to state which of the various known p-electron hyperfine interactions is dominant. Note however that p core polarization alone cannot account simultaneously for $\mathcal{K}^{69,71}$ and R_M^{71}/T if the Korringa relation of Eq. (9) is to be obeyed. For a Knight shift $K_p = -0.133\%$ we find that the expected core-polarization relaxation rate is $R_p/T \approx 0.21$, nearly an order of magnitude smaller than the observed value. It does not seem likely that dipolar hyperfine interactions (which do not contribute to $\mathcal{K}$ in a cubic metal) are large enough to account for this discrepancy. The remaining possibilities are the short- and long-range orbital interactions and the presence of a small s-electron effect at 4.2 K. There seems to be no clear way of distinguishing between these various possibilities on the basis of the available experimental information.

The susceptibility at $T=0$ is diamagnetic, primarily because of the ionic contributions. Hartree–Fock calculations by Hurd and Coodin[36] yield values of $\chi_i = -3.62\times10^{-5}$ emu/mol for the Au^+ ion and -0.954×10^{-5} emu/mol for the Ga^{+3} ion. The net ionic diamagnetism for $AuGa_2$ based on this calculation is therefore -5.53×10^{-5} emu/mol, which is nearly equal to the measured value. Now a rough calculation of the electronic contribution assuming 28 free (noninteracting) electrons per unit cell gives a Pauli–Landau susceptibility of 2.48×10^{-5} emu/mol for $m^*/m_0 = 1$ in Eq. (2). This value is of course much larger than the difference between the observed value of χ and the calculated ionic contribution and the discrepancy increases if electron-electron enhancement is included. This effect may suggest near cancellation of the paramagnetic and diamagnetic terms in χ_e or, equally likely, the discrepancy may simply reflect inaccuracies in the theoretical values of χ_i. We shall return to this point shortly.

We next consider the situation for the Pd alloy at 4.2 K. Both the Knight shift and magnetic relaxation rate show large increases relative to $AuGa_2$. This implies that the states at the Fermi level have substantial s character, as might be expected if the Fermi level now lies in the formerly filled Ga-s antibonding band.[7] These observations are consistent with those of Wernick *et al.*,[2] who found that the magnetic susceptibility, superconducting transition temperature (T_c), and linear coefficient of specific heat (γ) all exhibited substantial increases with addition of up to 5-at.% Pd. For higher Pd concentrations little additional change in these quantities was observed.

The change in susceptibility on alloying with Pd indicates a substantial (paramagnetic) increase in χ_e. For a 5% alloy, the total ionic susceptibility is calculated to be $\chi_i = -5.48\times10^{-5}$ emu/mol, where for Pd we have used the value $\chi_i = -2.6 \times10^{-5}$ emu/mol obtained by Seitchik *et al.*[37] The total ionic susceptibility is therefore only slightly affected by alloying, so that the observed increase of 1.7×10^{-5} emu/mol must reflect a corresponding increase in χ_e. This result, taken with the increases in $\mathcal{K}$, T_c, and γ, points to an increased value of $N(E_F)$ on alloying with Pd.

The effect of Pd alloying on $\mathcal{K}^{69,71}$ has features suggestive of both a local and nonlocal character. On the other hand, the position of the resonance line *center* suggests nonlocal behavior. For a random distribution of Pd on the Au lattice with average concentration 5%, it is easily shown that roughly 82% of the Ga sites have *no* near-neighbor Pd atoms. About 60% of the sites have neither first- nor second-neighbor inpurities. Thus if alloying affected the $\mathcal{K}$ values of only those Ga sites near an impurity, most of the intensity of the low-temperature Ga spectrum would lie near the resonance position for pure $AuGa_2$. This is clearly not consistent with the spin-echo spectrum shown in Fig. 3. Rather, the experiment shows that a few percent of Pd produces a large increase in s character at a majority of Ga sites.

The behavior of the linewidth in the Pd-doped sample, on the other hand, suggests that some dependence on the local Pd concentration is important. The fact that the width of the spin-echo spectrum is proportional to magnetic field indicates that the principal line broadening mechanism is a distribution of local Knight shifts. Furthermore, as a function of temperature, we observed that the linewidth scales roughly with the *difference* in resonance position of the Pd alloy and pure $AuGa_2$. We conclude, therefore, that addition of Pd produces an over-all change in Knight shift for all nuclei but that an additional effect due to local Pd concentration is superimposed on the average shift.

One nonlocal effect that is likely to be important is the average reduction in lattice constant produced by Pd alloying. The percentage change in a 5% alloy sample relative to pure $AuGa_2$ is comparable to that achieved with 6 kbar external pressure on $AuGa_2$. This corresponds to a movement of the Ga-s-band edge 0.01–0.02 eV closer to the Fermi level according to the calculation made by Schirber and Switendick.[13] Thus, if the Fermi level is as close to the s-band edge as the pressure experiments suggest, it is likely that at least part of the average change of $\mathcal{K}^{69,71}$ with alloying results from volume effects.

Another nonlocal effect which could conceivably play a role is a simple rigid-band lowering of the Fermi level into the s band by substitution of Pd ($4d^{10}$) for Au($6s^1$). For a total $N(E_F)$ close to the free-electron value, we find that 5 at. % Pd should lower E_F by 0.03–0.04 eV according to this model. In the case of either pure volume or rigid-band effects the observed linewidth could result from modulation of the local band-edge position by lattice strains.

2. *Properties at T_m*

Before discussing the temperature variation of the magnetic properties of $AuGa_2$, we consider the situation in the immediate vicinity of the melting point. From the results given in Figs. 2 and 5 it may be seen that $\mathcal{K}^{69,71}$ and R_M^{71}/T change only slightly on melting compared with the changes which occur at lower temperatures. Such small melting-point changes strongly suggest that the density of states and wave functions in the solid near T_m are not very different from those in the liquid.

Now there is considerable evidence that the electronic structure of metallic liquids [i.e., electrical conductivity greater than about 10^4 $(\Omega\,\mathrm{cm})^{-1}$] is quite well approximated by that of a free-electron gas.[38] The Hall coefficient, in particular, indicates that $N(E_F)$ is close to the free-electron value for liquids of this class.[39,40] Calculations of the Knight shift, such as that done by Kasowski[41] for Cd, indicate a free-electron-like liquid even where the solid density of states deviates significantly from the free-electron value. In the case of liquid $AuGa_2$, the electrical conductivity value [17 000 $(\Omega\,\mathrm{cm}^{-1})$] agrees well with the prediction of the Faber–Ziman theory based on the free-electron model.[42] We suggest, therefore, that the small changes observed in $\mathcal{K}^{69,71}$ and R_M^{71}/T represent evidence that the electronic structure of the *solid* near T_M is also close to that of the free-electron gas. (This line of reasoning is essentially that taken by Ziman,[43] who has considered the small changes of $\mathcal{K}$ at T_M observed for a number of metals.) The observed insensitivity of $\mathcal{K}^{69,71}$ and R_M^{71}/T to alloying with Pd, In, or Al at 300 K and above, and the observation that the Korringa enhancement $K(\alpha)$ is unchanged on melting, add further support to the picture of only a slight additional smoothing of the density of states on passing from the solid to the liquid state.

It might be argued that small changes of $\mathcal{K}^{69,71}$ and R_M^{71}/T at T_M imply that the electronic structure of the liquid resembles that of the solid because of preservation of local order in the liquid state. This point of view, the converse of that just developed, would suggest that the sharp structure associated with the Ga-s band remains intact in the liquid. We consider this prospect highly unlikely for the following reasons. First, the density of $AuGa_2$ was observed[44] to *increase* on melting, which suggests collapse of the fluorite structure to one of denser packing. In most cases in which low-coordinated solidlike order is believed to persist through melting, the density *decreases* on fusion.[45] Second, in the conductivity data for liquid Au-Ga alloys,[42] there is no evidence for any clustering or compound formation at the composition of $AuGa_2$. Third, the values of $\mathcal{K}^{69,71}$ and R_M^{71}/T are independent of temperature over a wide range of temperature in the liquid. One would expect local-order effects to be altered significantly well above T_m. Finally, since the constant-energy surfaces must be spherical, the highly anisotropic low-temperature Ga-s band must necessarily be changed appreciably in the liquid. We conclude, therefore, that evolution of an isotropic and free-electron-like band structure occurs almost entirely in the solid state as the temperature is raised.

The single magnetic property that does change appreciably at T_m is the total susceptibility. The values of χ_m for pure $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$ increase at T_m and attain the same value in the liquid range. In light of the small *decreases* in $\mathcal{K}^{69,71}$ and R_m^{71}/T at T_m, it is clear that the change in χ_m cannot result from an increase of the paramagnetic spin susceptibility χ_e^p. Rather, this effect must reflect reductions of the electronic and/or ionic diamagnetism related to the structural changes occurring on fusion. These changes in χ_m are, however, roughly 3–10 times larger than observed in simple fcc metals.[46] The behavior of the diamagnetic susceptibility in the solids clearly cannot be easily explained on the simple band-smearing model suggested above and this presents, as we shall see, a recurring difficulty.

On the other hand, the equality of χ_m for liquid $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$ is in agreement with the notion that the electronic structure of the liquid is very close to a free-electron-gas situation. In this connection, it is interesting to note that the observed value of χ_m (-3.1×10^{-5} emu/mol) is almost precisely equal to the sum of the calculated ionic diamagnetism and the Pauli–Landau free-electron susceptibility. A similar statement can be made for $AuIn_2$. This result must be viewed with caution, however, because there is no apparent reason why exchange enhancement of the Pauli susceptibility should be absent and the inclusion of a typical enhancement factor $[(1-\alpha)^{-1}\sim 1.5-2.0]$ would raise the calculated susceptibility by some

2×10^{-5} emu/mol above the observed value. This discrepancy is comparable to that found in the calculation of the low-temperature susceptibility and this may indicate that the theoretical values of χ_i for Au^+ are too small in absolute value by roughly 2×10^{-5} emu/mol. Such an error would affect the calculations for all samples and temperatures equally.

3. *Properties in the Range $4.2 \leq T \leq 400$ K*

We turn our attention next to the pronounced temperature variation of the magnetic properties and consider first the range $4.2 \leq T \leq 400$ K. The data for χ_m, $\mathcal{K}^{69,71}$, and R_M^{71}/T are summarized schematically in the upper section of Fig. 9. The sharp increases in $\mathcal{K}^{69,71}$ and R_M^{71}/T are generally held to reflect increases in the Ga-*s* character at the Fermi level resulting from partial depopulation of the Ga-*s* antibonding band. As stated previously, this band is believed to be full (or very nearly so) at 4.2 K. The more normal behavior of $AuIn_2$ and $AuAl_2$ then follows from the fact that the band in question intersects the Fermi level at all temperatures in these metals.

There are several mechanisms which are potentially capable of causing an increase in Ga-*s* character as the temperature increases. Switendick and Narath originally suggested that thermal expansion might shift the Ga-*s* band upward toward the Fermi level. However, the pressure experiments of Schirber and Switendick[13] make this suggestion somewhat untenable. By studying the pressure dependence of the second-zone hole surface in $AuAl_2$ and $AuIn_2$, those workers concluded that expansion of the lattice (i.e., raising T) should *increase* the gap between the *s*-band edge and the Fermi level. The sign of this volume dependence was also verified by direct calculation of the band positions at different lattice constants.

Another possibility suggested by Switendick and Narath[7] is that the Fermi level is extremely close to the top of the Ga-*s* band at $T=0$ and that thermal depopulation of this band produces the observed increase in Fermi-level *s* character. An apparent difficulty with this proposal is that it requires E_F to be within ~0.02 eV of a very sharp piece of structure in the density of states. While perhaps somewhat surprising, this fortuitous placement of the Fermi level is not impossible and it is certainly supported by the Pd-alloy data and the pressure experiments discussed earlier.

An additional mechanism that we suggest may also be important is phonon modulation and displacement of the band structure and the concomitant shifting of Ga-*s* density of states relative to the Fermi level. Since the Debye temperature is about 200 K for $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$, we might expect phonon effects to play a significant role for $0 < T < 400$ K. A detailed calculation of the temperature-dependent band structure using a Debye–Waller factor to reduce the effective ionic pseudopotentials has not been attempted. However, the success of Kasowski and Falicov[41,47] in explaining the temperature-dependent Knight shift in cadmium using a similar technique may indicate that such a calculation is warranted. We have used here a very simple approach to estimate the effect of phonons on the band structure. Schirber and Switendick[13] found that a 1% contraction of the lattice constant shifts the calculated Ga-*s*-band edge by *at least* 0.07 eV relative to the Ga-*p* bands. Now we know that at 100 K the rms ionic displacement is approximately[48]

$$(x^2)^{1/2} = (9\hbar^2 T/Mk\Theta_D^2)^{1/2} \cong 0.03d \text{ (at 100 K)}, \quad (10)$$

where M is the (average) atomic mass and d is the Ga-Ga separation. Hence from Schirber and Switendick's calculation we might expect a phonon modulation of the band edge by approximately 0.2 eV, which is about the same as the calculated width of the upper edge of the Ga-*s* band $(\Gamma_{2'} - X_3)$.[49] This suggests that appreciable smoothing of the density of states occurs on the time scale of the nuclear Larmor frequency, which is several orders of magnitude smaller than characteristic phonon frequencies.

The role of the phonons in this problem is further underscored by the sound velocity measurements of Testardi,[50] who found an unusual softening of two of the elastic moduli (c_{11} and c_{12}) in the same range in which the magnetic properties are changing most rapidly with temperature. Likewise, the unusual behavior of the thermal expansion coefficient of $AuGa_2$, $Au_{0.95}Pd_{0.05}Ga_2$, and $AuIn_2$ indicates that the anharmonic properties of these materials differ significantly from Cu, Au, and $AuAl_2$. The unique behavior of $AuAl_2$ correlates with the suggestion made by Carter *et al.*[8] that for this compound the Fermi level lies below the main peak in the density of states. Thus, in the temperature ranges where the onset of thermal expansion occurs, $AuAl_2$ is the only case in which the Fermi level does not lie near a peak in the *s*-band density of states.

The Pd-alloy $\mathcal{K}^{69,71}$ data can also be interpreted in terms of a phonon-modulated band edge. In this case the Fermi level falls just at the upper edge of the *s* band at 4.2 K. Thus, lattice vibrations will, on the average, reduce the value of $\mathcal{K}^{69,71}$ as the temperature rises. Eventually, the structure becomes sufficiently smeared that the difference between $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$ becomes negligible and the shifts converge to a common high-temperature value for both systems.

We now proceed to a somewhat more quantitative discussion of these speculations. It will first be necessary, however, to affect a separation of $\mathcal{K}^{69,71}$ into distinct contributions from *s*- and *p*-like con-

TABLE IV. AuGa$_2$ s-electron $\mathcal{K}^{69,71}$ contributions, corresponding Korringa relaxation rates, and experimental Korringa correction factor $K(\alpha)$ for $\beta = 0.2$ in Eq. (11).

T (K)	$\mathcal{K}_s(T)$ (%)	$R^{71}_{M,s}/T$ (sec K)$^{-1}$	$K(\alpha)$
4.2	0.0	0.0	...
20	0.008	0.0023	...
78	0.170	1.02	...
195	0.524	9.74	0.79 ± 0.04
300	0.587	12.18	0.71 ± 0.02
400	0.607	12.98	0.67 ± 0.02
600	0.611	13.19	0.52 ± 0.03
765	0.611	13.19	0.49 ± 0.03

duction electrons. For simplicity we employ a slightly generalized version of the model suggested by Jaccarino *et al.*[1] We write

$$\mathcal{K}^{69,71}(T) = \mathcal{K}_s(T_m) D(T) + \mathcal{K}_p(0)\,[1 - \beta D(T)]. \tag{11}$$

If we specify that $D(T)$ for AuGa$_2$ be a monatonically increasing function of temperature with $D(0) = 0$ and $D(T_m) = 1$, then we convert the general expression given in Eq. (11) into a specific model that explicitly assumes that the *entire* $T = 0$ contribution comes from p-state effects and $\mathcal{K}_p(0) = -0.133\%$. As mentioned earlier, there is no compelling support for this assumption, but for simplicity we shall make it here.

Next we must specify the parameter β which determines the change in p-state contribution with increasing temperature. Jaccarino *et al.*[1] assumed $\beta = 1$, which is equivalent to requiring a complete transition from p to s character at the Fermi level. Experimental evidence, however, points to a somewhat different assumption. Switendick and Narath[7] state that the bands which intersect the Fermi level at 0 K in AuGa$_2$ are composed of states with Ga-p and Au-s character. They further reported that the gold Knight shift $\mathcal{K}^{197}$ showed only a modest decrease between 4.2 and 232 K. This experimental result implies, indirectly, that the Ga-p character at E_F is not strongly temperature dependent, but that $\mathcal{K}_p^{69,71}(T)$ might be expected to decrease by approximately 20% in the temperature range $0 < T < 300$ K. Above 400 K the Knight-shift data indicate no significant temperature variation in either s or p contributions. If we then take $\beta = 0.2$ (Table IV) and require $D(400) \cong 1$, Eq. (11) implies $\mathcal{K}_s(T_m) \cong 0.611\%$ and we can rewrite Eq. (11) as

$$\mathcal{K}^{69,71}(T) = 0.638\, D(T) - 0.133. \tag{12}$$

This relation, of course, simply defines $D(T)$ subject to the above assumptions. However, since $D(T)$ specifies the temperature variation of the s contribution to $\mathcal{K}^{69,71}$, Eq. (12) enables us to compare model calculations with the experimental $D(T)$ tabulated in Table V. An expression similar to Eq. (12) can be written down for the Pd-alloy results providing we *assume* a constant value $\mathcal{K}_p = -0.133\%$. For the alloy system the experimental $D(T)$ decreases from $D(0) \cong 1.46$ to $D(T_m) = 1$ as shown in Table V.

We next consider briefly a very simple calculation of $D(T)$. It is worth emphasizing at the outset that this exercise is intended only to illustrate that a simple model can reproduce the major features of the experimental results, and in no sense does it represent an accurate theoretical calculation. We shall postulate a step function s-electron density of states with band edge at E_0 and, in order to simulate phonon modulation effects, we shall allow this band edge to move to higher energy with increasing temperature as

$$E_0(T) = E_0 + 2kTE_1. \tag{13}$$

This model, with E_1 taken equal to zero, is the rigid-band thermal-excitation model originally suggested by Switendick and Narath and applied here to a specific form of $N(E)$. The s contribution to the Knight shift can be written by recasting Eq. (4) in the form[51]

$$\mathcal{K}_s = \frac{8\pi}{3} \langle |\Psi(0)|^2 \rangle_F \tfrac{1}{2}\gamma_e^2 \hbar^2 \times \left[-\frac{1}{4kT} \int N_S(E) \operatorname{sech}^2\!\left(\frac{E - E_F}{2kT}\right) dE \right], \tag{14}$$

and with our model density of states $N_S(E)$, we obtain $D(T)$ by straightforward integration:

$$D(T) = \frac{1 + \tanh(E_1 - \Delta/2kT)}{1 + \tanh E_1}, \tag{15}$$

with $\Delta = E_F - E_0$.

Results for two calculations of $D(T)$ with various choices for the parameters Δ and E_1 are shown in Figs. 10 and 11 and the experimental results for pure AuGa$_2$ and for Au$_{0.95}$Pd$_{0.05}$Ga$_2$ are also indicated. We can draw several general conclusions from these results and other similar calculations. First, there is semiquantitative agreement between this crude model calculation and the experimental results for both pure and Pd-doped material. The actual Ga-s density of states will differ from our step-function model in having structure, pos-

TABLE V. Experimental values of the function $D(T)$ for AuGa$_2$ and Au$_{0.95}$Pd$_{0.05}$Ga$_2$ obtained from Eq. (11) as described in the text.

	D (T)	
T (K)	AuGa$_2$	Au$_{0.95}$Pd$_{0.05}$Ga$_2$
4.2	0.0	1.46
20	0.013	...
78	0.279	1.20
195	0.860	0.96
300	0.961	1.00
400	0.992	1.01
600	1.000	1.01
765	1.000	1.00

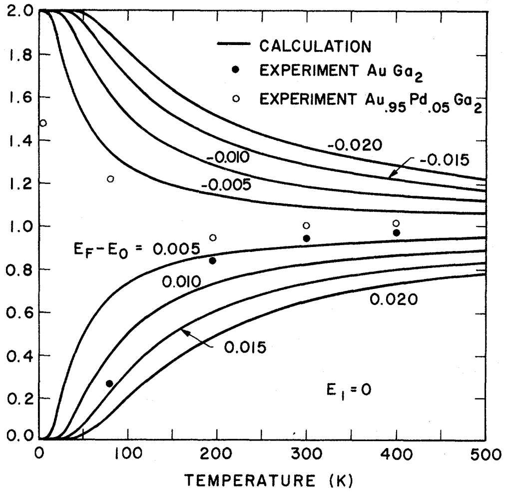

FIG. 10. The function $D(T)$ vs temperature computed from Eq. (15) of the text. Results for various values of $\Delta = E_F - E_0$ (in eV) are shown. The parameter $E_1 = 0$ [Eq. (13)] and hence the band edge remains fixed at E_0. Experimental values of $D(T)$ obtained from Eq. (11) are indicated for AuGa$_2$ and Au$_{0.95}$Pd$_{0.05}$Ga$_2$.

sible tailing of the band edge, and a finite band width. We have carried out a number of calculations using more sophisticated models for $N(E)$ and the results are similar to those we have illustrated. Ideally one would like to use the $N(E)$ obtained from a detailed band-structure calculation but we do not anticipate that the results would be particularly more revealing than those we have given. Second, to obtain a rapid rise of $D(T)$ with temperature it appears necessary that at $T = 0$, the Fermi level lie very close to the band edge E_0, on the order of 0.02 eV or less. And finally, a very small band motion on the order of 0.01 eV per 100 K evidently improves agreement with experiment for both pure and doped material. More pronounced band motion leads to less satisfactory agreement with experiment, especially for the Pd-alloy results.

To summarize, we find that a very simple model can account for the major features of the Knight-shift results. It should be noted that while the model calculation for the Pd alloy employs rigid-band concepts for simplicity, the qualitative features of the results would not be significantly altered by introduction of band-edge smearing on the scale of roughly 0.020 eV. One would hope that inclusion of detailed features of $N(E)$ and thermal band modulation would reduce the discrepancies remaining in the temperature dependence and, conceivably, explain the observed dip in $D(T)$ around 200 K for the Pd alloy.

The relaxation data is considerably more difficult to interpret because the decomposition of R_M^{71} into s and p contributions cannot be carried out without introducing a number of additional, and presently indefensible, assumptions. We can, however, remark that since we expect the s contribution to obey an approximate Korringa relation, there will at least be a contribution to $R_M^{71}(T)/T$ having roughly the temperature dependence illustrated in Fig. 5. Additional temperature dependence will certainly enter because of the p contributions, but we have no detailed procedure for analyzing these terms separately.

The susceptibility variation in the range $0 < T < 400$ K remains a persistent enigma. Both AuGa$_2$ and Au$_{0.95}$Pd$_{0.05}$Ga$_2$ become substantially more diamagnetic as T increases and the temperature dependence for both materials is similar even though the corresponding Knight shifts are dramatically different. If a Ga-s density of states is uncovered as temperature rises according to the model proposed above, we would expect increased electronic paramagnetism and perhaps a *small* electronic diamagnetization (due to the flat band and large m^*), rather than the enhanced diamagnetism which is observed. The traditional $\mathcal{K}$-vs-χ plots are not particularly instructive because they yield an anomalous negative slope[1] for AuGa$_2$ and a positive slope for Au$_{0.95}$Pd$_{0.05}$Ga$_2$. We can only concur in the suggestion made by Carter *et al.*[8] that some additional diamagnetism of unknown origin is "turned on" as the Ga s-band is exposed and that this diamagnetism swamps the increased spin paramagnetism indicated by the rising Knight shift.

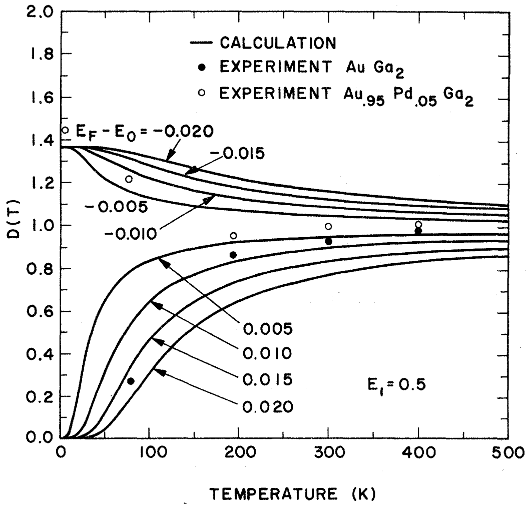

FIG. 11. The function $D(T)$ vs temperature computed from Eq. (15) and with various values of $\Delta = E_F - E_0$ (in eV). The parameter $E_1' = 0.5$ [Eq. (13)] implies a band-edge motion of approximately 0.01 eV per 100 K. Experimental values of $D(T)$ are indicated.

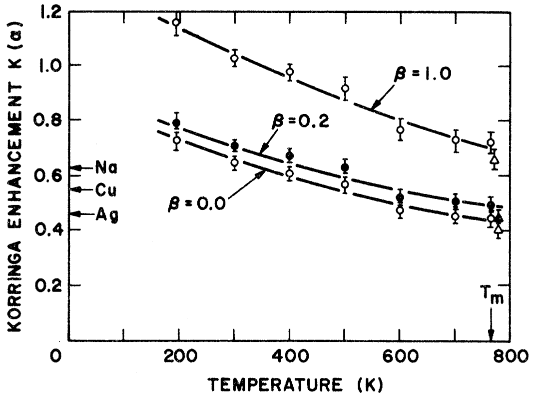

FIG. 12. Korringa enhancement factor $K(\alpha)$ obtained from experimental Knight shifts and magnetic relaxation rates using Eq. (11) with different values of the parameter β. The highest temperature points (triangles) refer to the liquid with the assumption that p-electron contributions are unchanged across the melting transition. As explained in the text we believe a value of approximately $\beta = 0.2$ to be the most appropriate choice. Also shown, for comparison, are experimental values of $K(\alpha)$ for the pure metals Na, Cu, and Ag.

4. Properties in the Range $400\,\mathrm{K} \leqslant T \leqslant T_m$

The principal effects to be explained in this temperature range are the pronounced decrease of R_M^{71}/T and strong variations of χ_m for AuGa$_2$ and Au$_{0.95}$Pd$_{0.05}$Ga$_2$ in the presence of temperature-independent Knight shifts. The observed constancy of $\mathcal{K}^{69,71}$ is consistent with our earlier contention that these materials become nearly-free-electron-like as T approaches T_m. The behavior of the relaxation rates and susceptibilities, however, appears to contradict this hypothesis.

From the Knight-shift decomposition described by Eq. (12), we find that for $T \gtrsim 200$ K,

$$\frac{R_{M,p}}{R_{M,s}} \approx \left(\frac{\mathcal{K}_p}{\mathcal{K}_s}\right)^2 \lesssim 0.04, \tag{16}$$

and we may safely assume that all the observed relaxation above this temperature is due to s-electron effects alone. Thus, from the Korringa relation of Eq. (6) we would expect $R_{M,s}^{71}$ to remain independent of temperature, contrary to the experimental observation. Now, since the band-structure calculations suggest sharp structure in the density of states, one might anticipate unusual temperature dependence for $R_{M,s}^{71}/T$ if the Fermi level lies on, say, a peak whose width is comparable to kT. We have investigated this possibility by inserting model functions $N(E)$ having this feature into calculations such as those for $D(T)$ described in Sec. IV B 3. We were unable to find any suitable form of $N(E)$ that would produce both a maximum in $R_{M,s}^{71}/T$ and a saturated temperature-independent value of $\mathcal{K}_s^{69,71}$. We concluded from this that the relaxation data cannot be explained fully in terms of structure in the density of states and, accordingly, have turned our attention to the effects of temperature on the electron-electron enhancement factor $K(\alpha)$.

We have extracted experimental values of $K(\alpha)$ at various temperatures by assuming (i) that $R_{M,s}^{71} = R_M^{71}$ above 200 K and (ii) that $\mathcal{K}_s^{69,71} = (0.611)D(T)$, as discussed earlier. The results, plotted in Fig. 12, show a smooth decrease of $K(\alpha)$ from 0.78 at 200 K to 0.49 at T_m. If we had made a different assumption about the temperature dependence of the p-electron term (i.e., a different choice of β) the absolute value of $K(\alpha)$ would be changed appreciably, but the relative variation with temperature would be preserved (Fig. 12).

A theoretical expression for the enhanced susceptibility of a free-electron gas was given in Eq. (7). This result seems quite adequate for explaining the Korringa enhancement of a monovalent free-electron metal such as Na.[23,52] However, for AuGa$_2$ a number of complicating factors enter and these necessitate more careful examination of the enhancement effects. In particular, we must take into account that as the Ga-s-band states are exposed both the s-band density of states (and hence α) and the distribution of these states in k space will change with temperature. As a result, both the static enhancement factor α and the Korringa enhancement function $K(\alpha)$ will be temperature dependent. We wish to consider whether these effects can account for the observed temperature dependence of $K(\alpha)$.

When the states at the top of the Ga-s band are first exposed, one has a highly unusual situation in which the s electrons that dominate $\mathcal{K}^{69,71}$ and R_M are concentrated at a few special points in the Brillouin zone. According to the free-electron Fermi surface described by Jan *et al.*,[4] the Ga-s band (second-zone hole surface) first appears as a small octahedral piece centered at Γ. In an extended-zone picture, these states lie on small regions centered around the L directions on the free-electron Fermi sphere. Now as the temperature increases, more of these states are uncovered and the corresponding pieces of Fermi surface must grow in order to accommodate the additional s electrons. Above 400 K the constant value of $\mathcal{K}$ implies that the total number of s electrons is no longer changing. Thus any further smoothing of the band structure can only lead to redistribution of the s states from the pockets to achieve the isotropic distribution characteristic of the liquid state. The various stages of this process are indicated schematically in Fig. 13.

Yafet has performed an interesting calculation which is germane to the situation just described.[53]

He considers a two-band model in which one has s and p electrons that interact both with their own species and with the other. Only the s electrons, however, respond to the field of the nuclear spins. He finds that the enhanced susceptibility of the s electrons may be written in the form

$$\chi_s(q,\omega)=\chi_s^0(q,\omega)\Big/\left\{1-\left[\frac{2u}{\gamma_e^2\hbar^2}+\left(\frac{2J}{\gamma_e^2\hbar^2}\right)^2\frac{\chi_p^0(q,\omega)}{1-(2v/\gamma_e^2\hbar^2)\,\chi_p^0(q,\omega)}\right]\chi_s^0(q,\omega)\right\}\ , \qquad (17)$$

where $\chi_s^0(q,\omega)$ and $\chi_p^0(q,\omega)$ are, respectively, the unenhanced s- and p-electron susceptibilities, u and v are the intra-atomic s- and p-electron Coulomb integrals for a δ function interaction $[V(q)=\text{const}]$, and J is the s-p exchange integral. It is clear that for $J=0$, Eq. (17) reduces to Eq. (7) for the s electrons alone. However, the presence of the p-electron exchange field leads to an additional enhancement whose q dependence is determined by the enhanced p-electron susceptibility $\chi_p(q,\omega)$.

Now, as the temperature increases, two main effects will occur. First because the s-electron density is increasing, there will be an increase in $\chi_s^0(0,0)$, which leads to changes in the static enhancement α and also $K(\alpha)$. Thus, the s-electron effects alone should lead to an increase in α and corresponding decrease in $K(\alpha)$ with increasing T. This effect certainly occurs in the range $T \lesssim 400$ K where $\mathcal{K}_s$ rises rapidly with increasing T. It cannot, however, account for the decrease in $K(\alpha)$ above 400 K since $\mathcal{K}_s$ and, presumably, $\chi_s(0,0)$ and α are constant in this range.

The second effect relates to the p-electron exchange term in the denominator of Eq. (17). Consider first the situation at temperatures sufficiently low that the dimensions of the second-zone hole surface are small compared with the free-electron wave vector k_F. Then all q values connecting s states in this piece will be small compared with the typical values connecting *p states* on the remainder of the Fermi surface. The enhancement of $\chi_p(q,\omega)$ and, consequently, the effect of the s-p exchange term will therefore be maximum for these small q values. At higher temperature, the s-state piece is larger, the typical q values are increased, and the enhancement from $\chi_p(q,\omega)$ is reduced. The net result of this effect is that the enhancement of R_M/T is reduced by the s-p exchange term at high temperatures. On the other hand, as Yafet points out,[53] the enhancement of $\mathcal{K}$ does not reflect these changes in Fermi-surface geometry since the q dependence of $\chi_p(q,\omega)$ does not enter. Thus, so long as the total number of s electrons is constant, we can have a constant value of $\mathcal{K}$ in the presence of a temperature-dependent $K(\alpha)$ produced by the redistribution of the s states in k space.

The main effect of Pd alloying is to drop the Fermi level into the Ga-s band at low temperatures. At high temperatures ($T>400$ K) the critical features of the density of states are sufficiently smeared that small changes of E_F and volume due to alloying no longer have much effect on Ga-s susceptibility. It is not surprising, therefore, that the enhancement behavior of R_M^{71}/T is nearly the same for $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$.

Finally, we consider the high-temperature susceptibility results. As was true in the low-temperature range, the susceptibility remains the most poorly understood aspect of the $AuGa_2$ dilemma. The dramatic increase in χ_m above 550 K clearly originates in either χ_i or χ_e^d; otherwise we should see some reflection of this effect in the temperature dependence of $\mathcal{K}^{69,71}$. Of these two possibilities, it is more reasonable to attribute the effect to decreasing electronic diamagnetism (χ_e^d), which depends rather critically on the details of the band structure. It is suggestive that the trend of χ_m is

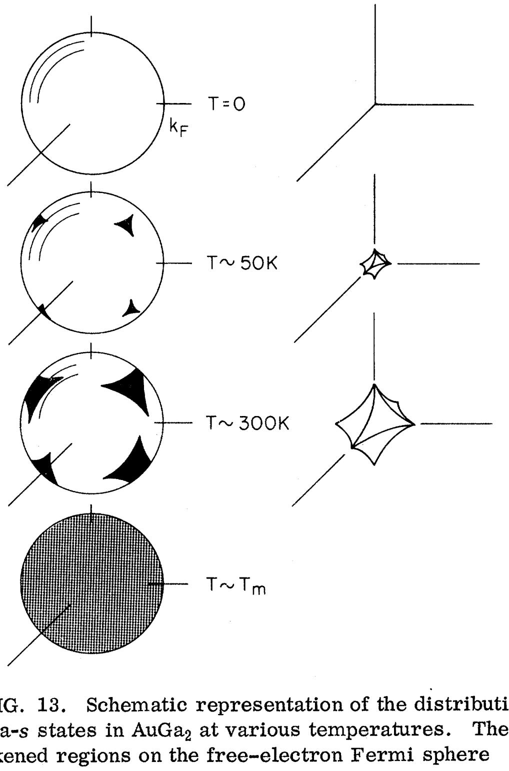

FIG. 13. Schematic representation of the distribution of Ga-s states in $AuGa_2$ at various temperatures. The darkened regions on the free-electron Fermi sphere (left) represent Ga-s states. The corresponding pieces of Fermi surface in a reduced-zone representation (right) are as described in Ref. 4.

in the direction of the liquid value which, as we have pointed out, is consistent with free-electron paramagnetism and diamagnetism. One possibility is that the electronic diamagnetism is reduced as the *s* electrons redistribute themselves isotropically on the Fermi sphere. We hasten to point out, however, that the results for $Au_{0.95}Pd_{0.05}Ga_2$ do not show this effect in χ_m, even though the relaxation data suggest similar modifications of the band structure in both pure $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$. It is obvious that we have not yet identified all the pertinent phenomena in the high-temperature range.

V. CONCLUSION

We have presented and discussed experimental data for the magnetic susceptibility, Knight shifts, magnetic spin-lattice relaxation rates, and lattice constants of $AuGa_2$, $Au_{0.95}Pd_{0.05}Ga_2$, and $AuIn_2$. We concur in the suggestions made previously[7,8,10-12] that the unusual temperature dependence of the magnetic properties of $AuGa_2$ arise from the presence of a Ga-*s* band whose extremely sharp upper edge lies just below the Fermi level at 4.2 K. We suggest that at higher temperatures this band becomes partially depopulated by the combined effects of thermal excitation across the Fermi energy and broadening of the sharp band edge by lattice vibrations. The importance of thermal broadening of the band features is emphasized by the fact that the changes in magnetic properties at T_m^- are much smaller than the temperature-dependent effects in the solid. We contend, therefore, that the electronic structure just below T_m is very close to the free-electron situation expected in the liquid state.

The temperature dependence of the lattice constants is normal in the sense that we observed no evidence of a phase transition in $AuGa_2$ between 4.2 and 700 K. Thus neither the low-temperature nor high-temperature anomalies can be associated with such an effect. We did however observe slightly unusual thermal expansion behavior in $AuGa_2$ and $AuIn_2$, while $AuAl_2$ expands in a manner more typical of fcc metals. This result suggests that the *X*-site *s* band plays a role in the anharmonicity of the lattice, a conclusion that may also be drawn from the behavior of the elastic constants in $AuGa_2$.

The magnetic relaxation rates continue to exhibit unusual behavior until close to the melting point. This suggests that redistribution in *k* space of the Ga-*s* electrons continues to change at very high temperatures even though, as evidenced by the Knight shift, the total *s*-electron density saturates at a constant value around 400 K. We have presented a qualitative explanation of the relaxation behavior based on temperature-dependent modifications of the electron-electron enhancement of the relaxation rate.

The temperature dependence of the magnetic susceptibility of $AuGa_2$ continues to defy explanation. Phenomenologically it can be said that the Ga-*s* band contributes a surprisingly large amount of electronic diamagnetism which "turns on" as the *s* band is first uncovered and then "turns off" at higher temperatures, where the *s* states finally distribute themselves isotropically on a free-electron Fermi sphere. The perplexing aspect of this is that we expect the Ga-*s* band to exhibit a high density of states (high m^*) and therefore to have only a small diamagnetism according to simple theory.

$AuIn_2$ is, by contrast with $AuGa_2$, a normal metal. Its properties are consistent with the conclusion reached from band-structure calculations[7] that the *s* band is broader and intersects the Fermi level at all temperatures. The NMR data in $AuIn_2$ bear out this general notion. We did, however, observe two unexpected effects in the susceptibility. The first is a peculiar overshoot of χ_m on melting and solidification. We can offer no explanation for this effect, which, to our knowledge, has not been observed in any other metal. The second effect is the gradual rise of χ_m between 200 K and T_m. This effect is smaller than, but suggestive of the high-temperature χ_m behavior of $AuGa_2$. It may well have a similar origin in the thermal evolution of a more free-electron-like band structure. The problem of temperature-dependent diamagnetism in the AuX_2 compounds clearly deserves further study.

ACKNOWLEDGMENTS

The authors are greatly indebted to the following people for stimulating discussions on various aspects of this work: B. Golding, V. Jaccarino, L. F. Mattheiss, A. Narath, P. Pincus, L. R. Testardi, J. E. Schirber, I. Weisman, and Y. Yafet. We acknowledge particularly the contribution of A. Narath, who first suggested to us the possible importance of unusual Fermi-surface effects in the electron-electron enhancement in $AuGa_2$. L. H. Bennett, J. E. Schirber, and A. C. Switendick kindly provided us with preprints of their work prior to publication. Expert technical assistance was provided by G. F. Brennert, J. V. Waszczak, D. Dorsi, and G. W. Hull.

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*Present address: Booz-Allen Applied Research, Inc., Bethesda, Md. 20014.

†Present address: Brown-Boveri Co., Baden, Switzerland.

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Spin Susceptibility and the Korringa Relation in a Two-Band Model

Y. Yafet

Bell Laboratories, Murray Hill, New Jersey 07974

(Received 6 June 1972)

The wave-number- and frequency-dependent spin susceptibility of a two-band (s and p) model with δ-function interactions is calculated in the random-phase approximation. The result shows that when the character of the s band changes with temperature, the Korringa product $(T_1T)^{-1}$ can be temperature dependent even when the Knight shift is not.

The experimental results reported in the preceding paper[1] show that in AuGa_2 at temperatures around 400 K the product of the relaxation rate T_1^{-1} of the gallium nuclei with the reciprocal temperature T^{-1} begins to decrease even though the corresponding Knight shift $\mathcal{K}$ remains constant. Warren *et al.*[1] conjectured that this departure from the (enhanced) Korringa relation could be understood in a two-band model, a s band and a p band, such that the two are coupled to each other by exchange,