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[13]The form of the curve in Fig. 2 suggests the presence of two mechanisms, the first having a large initial slope but saturating above 0.3-at.% Pt., and the second having an essentially linear behavior all the way to 5% Pt, but with a smaller slope. It is tempting to try to attribute these to the two mechanisms suggested in the text (i.e., relaxation and spin fluctuations), but further work is needed before a meaningful separation can be made.

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BAND STRUCTURE AND ^{197}Au NUCLEAR-MAGNETIC-RESONANCE STUDIES IN AuAl$_2$, AuGa$_2$, AND AuIn$_2$ *

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Measurements of the ^{197}Au Knight shift in AuAl$_2$, AuGa$_2$, and AuIn$_2$ are reported. In contrast to the strong temperature dependence of the ^{71}Ga Knight shift, only a weak temperature dependence of the ^{197}Au Knight shift in AuGa$_2$ is observed. Electronic energy-band calculations for these compounds yield differences which provide an improved model for interpreting these and other experimental results.

Considerable attention has recently been focused on the intermetallic compounds AuAl$_2$, AuGa$_2$, and AuIn$_2$.[1-4] This interest derives in part from the fact that samples with high residual-resistance ratios may be prepared, enabling Fermi-surface studies,[3-5] and in part from the unusual temperature dependence of the ^{71}Ga Knight shift in AuGa$_2$.[1] The lack of any temperature dependence of the ^{27}Al and ^{115}In Knight shifts in AuAl$_2$ and AuIn$_2$, respectively, coupled with electronic specific-heat[6] and de Haas–van Alphen (dHvA) Fermi-surface studies which "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"[1] constitutes the AuGa$_2$ dilemma. Although there seems to be evidence that AuGa$_2$ is in some way different (e.g., Knight shift, thermoelectric power[7]) from the other two, there are properties (dHvA orbits, F_1 and F_2 in the notation of Ref. 5) for which AuAl$_2$ appears dissimilar from the other two.

In this note we report two new results for this series of compounds: (1) experimental results for the ^{197}Au Knight shifts for all three compounds, and (2) preliminary results of band-structure calculations which give a consistent interpretation of many of the observed similarities and dissimilarities and which offer a significant improvement over the free-electron model, which predicts no significant differences between any of the compounds. We offer these preliminary results in the hope that they may aid further interpretation and as a basis for additional refinement of the model.

The ^{197}Au resonances were detected in 300-mesh powdered samples by means of spin-echo techniques. The 60-kOe external field was provided by a NbZr superconducting solenoid. Adequate signal-to-noise ratios were achieved by averaging the echo intensities with a Fabri-tek 952/1062 high-speed digital signal averager. Knight shifts were calculated from the experimental frequency/field ratios using the reference ratio $\nu/H = 0.072\,923$ kHz/Oe. At 1.2°K the resulting shifts for AuAl$_2$ and AuIn$_2$ were $(+0.94 \pm 0.05)\%$ and $(+1.49 \pm 0.05)\%$, respectively. For AuGa$_2$ we obtained the following values:

$$T = 1.2°K, \quad K = (+1.54 \pm 0.02)\%;$$

$$T = 4.0°K, \quad K = (+1.52 \pm 0.02)\%;$$

$$T = 27°K, \quad K = (+1.53 \pm 0.03)\%;$$

$$T = 76°K, \quad K = (+1.50 \pm 0.05)\%;$$

$$T = 232°K, \quad K = (+1.34 \pm 0.10)\%.$$

The absence of a strong temperature dependence for the ^{197}Au Knight shift is particularly noteworthy. In the same temperature range the ^{71}Ga shift is known to vary from -0.13% at 4°K to $+0.45\%$ at 230°K.[1] It follows that those states at the Fermi level which give rise to the positive ^{71}Ga Knight shift in the high-temperature region have little if any gold s character. The shifts in AuGa$_2$ and AuIn$_2$ have magnitudes which are similar to the shift in gold metal (1.65%).[8] In contrast, the AuAl$_2$ value is significantly smaller. We have also measured the ^{197}Au spin-lattice re-

FIG. 1. Energy bands for AuAl$_2$. Bands below 0.1 Ry are not plotted in directions W-K-Γ. Compatibility relations and straight lines are used to indicate the connectivity from W to K, similarly from L to W for those states not crossing the Fermi energy.

laxation rates in AuGa$_2$ between 1.3 and 4.0°K. The result, $T_1T = 3.4 \pm 0.6$ sec °K, is again similar to the metallic-gold value (4.6 sec °K).[8]

Nonrelativistic energy bands for the three compounds were calculated by the augmented plane wave (APW) method.[9] The potential was derived from a superposition of neutral atomic charge densities calculated by the Herman-Skillman[10] program. Energy eigenvalues were calculated at the equivalent of 128 points in the first Brillouin zone. Our results for AuX_2 (X = Al, Ga, and In) are shown in Figs. 1, 2, and 3, respectively. In all three figures the bands below 0.1 Ry are plotted only along the directions X-Γ-L-W; they are omitted in the directions W-K-Γ. These bands are well below the Fermi energy (E_F) and have a well-defined atomic character. The low-lying states $X4'$-$\Gamma1$-$L2'$-$W3$ can best be described as X-atom, s-like, valence-electron, bonding states between nearest-neighbor X atoms. The remaining states below 0.1 Ry are the gold $5d$ bands. The states $X3$-$\Gamma2'$-$L1$-$W3$-$K3$-$\Gamma2'$ are mostly X-atom, s-like, valence-electron, antibonding states between nearest-neighbor X atoms. The remaining bands near the Fermi energy are primarily composed of X-atom, p-like, valence-electron, bonding wave functions, together with a significant admixture of $6s$-like wave functions at the gold site. For

FIG. 2. Energy bands for AuGa$_2$ with same remarks as for Fig. 1.

all three compounds the first band is full. This is in agreement with the free-electron (FE) model. Ignoring the filled d bands (as does the FE model) we then have four filled or partially filled bands. The sixth band which in the FE model gives cigarlike shaped electron pockets centered around X is empty in our calculation for all three compounds.

For simplicity and ease of comparison we shall

FIG. 3. Energy bands for AuIn$_2$ with the same remarks as for Fig. 1.

cite only two features of our calculation, (1) the second-zone hole surfaces around Γ, and (2) the third-zone hole surfaces around L. We see both these features in Fig. 1 for $AuAl_2$. The hole surface about Γ is quite large; the linear distance Γ to the Fermi surface in the Δ direction is ~0.60 in units of π/a. The hole surface about L, however, is quite small, a typical linear dimension being on the order of 0.10. We see in Fig. 3 that our results for $AuIn_2$ are quite similar to those for $AuAl_2$, having a somewhat smaller hole surface about Γ and a much larger hole surface around L. In $AuGa_2$, on the other hand, the entire second band is below the Fermi energy and is filled, giving no contribution to the Fermi surface, although the band structure and Fermi energy are quite similar to those of $AuIn_2$ at the point L.

Thus, we see that the calculations give quite different results for $AuGa_2$ than for $AuAl_2$ and $AuIn_2$. In particular, the second-band hole surface which arises from gallium $4s$ valence electrons is missing. We now investigate whether these results are in agreement with the known experimental results and whether they allow a consistent interpretation. First, we consider the third-band hole surface about L. The de Haas–van Alphen results[5] gave very small orbits for $AuAl_2$ with larger and quite comparable orbits for $AuGa_2$ and $AuIn_2$. This agrees with our results described above. Our results for $AuAl_2$ and $AuIn_2$ give relative sizes for second-band hole orbits which agree with the de Haas–van Alphen results. We believe the calculated absence of second-band hole orbits in $AuGa_2$ is also in agreement with the de Haas–van Alphen results.[11]

Having gained some faith in the calculations, we now examine the predictions for the Knight shifts. We relate the positive X-site Knight shifts in $AuAl_2$ and $AuIn_2$ with the similar band structures and conduction-electron characters found at the Fermi energy. Contributions to the Knight shift from the s band give rise to a positive contact term, while those from the p bands give rise to a negative core-polarization term. Following Jaccarino et al., we assume for the p hyperfine field $H_{4p} \approx -\frac{1}{10}H_{4s}$ and conclude that the Knight shifts for $AuAl_2$ and $AuIn_2$ would be positive, in agreement with the experimental results. Furthermore, the absence of second-band positive s contributions explains the experimentally observed low-temperature negative Knight shift in $AuGa_2$. There is sufficient gold $6s$ character at the Fermi level in the p bands to account for the [197]Au shifts.

In order to explain the high-temperature positive Knight shift in $AuGa_2$ our argument becomes somewhat more speculative and inferential. To get a positive [71]Ga Knight shift we must gain gallium $4s$-like conduction-electron character at the Fermi surface. We note that the very flat band $\Gamma2'-\Delta2'-X3$, which is primarily gallium $4s$-like, lies ~0.1 Ry below the Fermi energy. Errors of this order of magnitude are not uncommon in "first-principles" band calculations.[12] We therefore arbitrarily adjust the band structure to place this flat band (high density of states) just below the Fermi energy. Thermal depopulation and/or changes in the position of the band due to thermal expansion effects are probable mechanisms for producing $4s$-band holes at the Fermi surface leading to positive contributions to the Knight shift. In addition to giving an explanation to the temperature dependence of the [71]Ga Knight shift, our model also explains the lack of a temperature dependence for the [197]Au Knight shift since the states being added to the Fermi surface are primarily gallium $4s$ (symmetry allows nothing less than d-like contributions at the gold site).

Several comments are relevant to our adjustment. Recent work[13] has shown that the superconducting transition temperature and electronic heat capacity of $AuGa_2$ increase markedly with the addition of small amounts of palladium. These results are both consistent with a large density of states just below the Fermi energy, since within the rigid-band model the Fermi energy drops with the substitution of Pd ($5s^0$) for gold ($6s^1$). The susceptibility at low temperature also becomes more positive upon the addition of Pd consistent with a positive spin paramagnetism from the second-band electrons. Our model is not successful in explaining the temperature dependence of the susceptibility, but the palladium experimental results show that this is less intimately involved with the density-of-states peak than are the specific heat and superconducting transition temperature.

We believe that our model offers considerable improvement over the free-electron model and should initiate further experimental work both to test and refine the model. In particular, experiments to establish the existence of second- and sixth-band surfaces would be useful.

Since the flatness of the $\Gamma2'-\Delta2'-X3$ band is related to the position of the gold d bands and to the position of the gallium $4s$ bonding band, experi-

mental information on the location of these bands
would be an important test of our model. This
flatness most likely would be destroyed if the
gold d bands were placed the 2 eV below the
Fermi energy needed to explain the optical prop-
erties. We do not believe that the gold d bands
are essential for an understanding of the optical
properties since the calculation gives a large
number of s-like and p-like states both above and
below the Fermi energy. Vishnubhatla and Jan[2]
arrived at a similar conclusion.

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EVIDENCE FOR AN OPTICAL TRANSITION AT A NONCENTROSYMMETRIC POINT
OF THE BRILLOUIN ZONE IN KI†

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The two-photon absorption spectrum of KI has been measured to 7.5 eV. The region
studied spans the spectral range in which all the prominent one-photon absorption peaks
reside. Our two-photon data exhibit two noticeable peaks at 7.21 and 7.375 eV. Based
on the parity argument and polarization dependence, we tentatively assign the peak at
7.21 eV to a $\Delta_6 \rightarrow \Delta_6$ transition.

A two-photon absorption spectrum was first
measured by Hopfield, Worlock, and Park[1] on
KI and CsI. Numerous other crystals have since
been studied by various investigators[2-7] using
similar techniques. However, the experimental
difficulties associated with inadequate continuum
sources in the ultraviolet region frequently
forced these studies to the limited region near
the fundamental absorption edges. Hence, this
powerful spectroscopic technique has not been
fully utilized to resolve controversies regarding
the structures observed in the optical spectra of
these crystals.

This Letter reports results of our two-photon

absorption measurements on KI extended to 7.5
eV, the region that contains all the prominent
one-photon structures. The experimental ar-
rangement was similar to one described earlier[7]
with the following important modifications: (a)
The uv probe light was imaged by an f:10 mirror
optics; (b) a solar-blind photomultiplier with a
LiF window was used as a detector; (c) a calcite
polarizer was inserted between the sample and
the monochromator; and (d) the oscilloscope
high-frequency bandpass was lowered from 50
to 7 MHz in order to eliminate excessive shot
noise.

Figure 1 shows our data, together with the