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Band-edge properties of a semiconductor alloy: An NMR study of $Hg_{1-x}Cd_xTe$

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We report ^{199}Hg NMR measurements of narrow-gap $Hg_{1-x}Cd_xTe$ alloys in the range $x=0.20$–0.28. By studying temperature dependences, we have identified intrinsic Knight shifts in these alloys. This provides a measure of Hg orbital contributions to conduction-electron states, and we find a consistently strong average contribution from Hg *s* orbitals. Furthermore, we identify local variations in the Knight shift with spatial variations in conduction-electron densities and symmetries. These characteristics have been related to randomly populated sites within the alloys. We also discuss ^{199}Hg chemical shifts and their relation to local orbital charges.

I. INTRODUCTION

Alloys of zinc-blende semiconductors are of great practical importance, since by composition changes, properties such as band gaps and lattice constants can be adjusted continuously. The macroscopic behavior of these alloys, however, depends strongly on atomic-scale structural and electronic variations; carrier mobilities and structural strengths both can be related to local configurations. Moreover, atomic ordering can readily occur under some growth conditions,[1,2] with a significant effect on band parameters.[3,4] In this paper we describe NMR studies of $Hg_{1-x}Cd_xTe$ alloys, focusing upon the Knight shift and shielding behavior as related to the local electronic characteristics.

NMR has been applied by a number of groups to II-VI and III-V alloys.[5–12] This spectroscopy provides one of the few local probes available for such studies, and a great deal of electronic structure information can be obtained in this way. Changes in chemical shift with alloy composition can provide a measure of charge transfer.[5,9] Furthermore, using modern spectrometers, the shifts of individual local configurations can be separated, and studies of local atomic ordering have been reported.[6,7,10,12] There has been little quantitative work with Knight shifts in semiconductor alloys, though, in large part because other mechanisms dominate the observable shifts. We have studied these shifts in the case of the ^{199}Hg resonance in $Hg_{1-x}Cd_xTe$, and will describe band-edge and charge transfer properties of these alloys.

The samples studied here are narrow-gap semiconductors, in the range $x=0.2$–0.3. This is the range of materials used for infrared detectors. HgTe itself is a semimetal, with valence and conduction bands touching at Γ, while the alloys are direct semiconductors when x exceeds 0.16. These alloys have been studied extensively,[13,14] and exhibit very low electron masses and high mobilities. Even though HgTe and CdTe bond lengths are nearly equivalent, studies have indicated a variation in bond character in their alloys.[15–17] Also, HgTe has opposite band-edge symmetry from that of CdTe, so that, for instance, *n*-type carriers in HgTe have *p* symmetry, while in CdTe and other direct-gap materials these states have *s* symmetry. This is responsible for the unusual electronic behavior in multilayers based on these materials.[18] We describe below how this symmetry change occurs locally, by examining the Knight shifts, after first discussing the relationship between the line shapes and local Hg-site environments. Finally, we also examine the chemical shift distribution, and its relation to bond charges.

II. EXPERIMENT

The samples studied here are single-crystal, solid-state-recrystallized specimens. We have studied two bulk compositions ($x=0.20$ and 0.28) and a liquid-phase-epitaxy (LPE) -grown sample of $x=0.22$. Bulk samples are 500 μm thick, while the LPE layers are 80–90 μm thick. In all cases, the samples obtained were Hg annealed for low-density *n*-type behavior, $n \le 10^{15}$ cm^{-3}. Transport measurements indicated that the $x=0.20$ sample (from the U.S. Army Night Vision Labs) had an electron mobility of approximately 1×10^5 cm^2/V s at 77 K, while quoted mobilities for the other two samples (from Texas Instruments) are in the same range. These are samples of good uniformity, and not heavily compensated.

We performed measurements in a standard home-built pulsed NMR spectrometer, with 9-T magnet, so that ^{199}Hg signals ($I=\frac{1}{2}$, $\gamma=7.590\,12$ MHz/T, 17% natural abundance) were observed near 68 MHz. Spectra were obtained from echo fast-Fourier transforms using a composite-pulse sequence, and digitally adding spectra obtained from two sides of the line to eliminate small sensitivity changes over the width of the lines. (The applied rf rotating field had an amplitude of 40 kHz, and off-resonance effects are a few percent at most in the final spectra.) The spin-lattice relaxation times (T_1's) we found to be about 1 min at room temperature, which did not appear to vary across the lines. Possible T_2 variations were not explored. Due to the long relaxation times and signal size, several days runs were summed to generate the spectra shown here.

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III. LINE SHAPES

Experimental line shapes for the two bulk samples are shown in Fig. 1. The line positions and structures for these spectra are related to local configurations in the alloy; the theoretical curves also shown in Fig. 1 are from a specific model described below. For the small LPE sample we have not obtained a detailed line shape for analysis, but have measured the center-of-mass line positions. The chemical shift dominates in all cases, but we will demonstrate that the Knight shift is significant as well, giving a measure of the band-edge states in these alloys. Moreover, with a model for the linewidths and shapes, we can extract information about the distribution of these states. Note that the ^{199}HgTe resonance frequency falls 450 ppm above the bare nuclear $\gamma=7.590\,12$ MHz/T,[5] and we see no resonance there for these samples. Also, the signal for possible Hg-metal inclusions would fall well outside the range studied.

Hg sites have four Te first neighbors, in the tetrahedrally bonded HgTe lattice. Differences in Hg- and Cd-atom occupation of the 12 next-nearest-neighbor sites in the alloy will thus be most important in determining the NMR shifts. Our spectra can be understood quite well with random atom counts within this second-neighbor shell. Distinct neighbor environments have been observed previously for anion resonances in $Hg_{1-x}Cd_xTe$ (Refs. 6, 7, and 10) and $Ga_xIn_{1-x}P$;[12] for the cation resonance, the number of configurations is greater, but we can still identify features that give rise to the line shape.

Our model relates the second- and, to a less extent, the fourth-neighbor shells to the chemical shifts. We assign increasing chemical shifts to Hg sites with an increasing number of Cd neighbors. This agrees with the trend for the average shift versus x,[5] and provides a consistent picture for our samples. For random occupation, the number of Cd second neighbors assumes a binomial distribution. We further distinguish configurations with the same number of Cd second neighbors according to the number attached to each of the four first-neighbor Te atoms. Random probabilities can readily be calculated: for instance, for two Cd second neighbors, two attached to the same Te (which we denote "0002") has a probability of 0.05 for $x=0.20$, while the two attached to different first neighbors (denoted "0011") has probability 0.23. Finally, fourth-neighbor counts are statistically significant for few Cd second neighbors: for instance, a lone Cd second neighbor has a 21% likelihood of having no further Cd neighbors in $x=0.20$ material.

Counting configurations in this way, we obtain a small number of local configurations that are statistically important. These are enumerated in Table I, where parameters used in the model curves are also given. For these curves, we superimposed equal-width Gaussian lines, weighted according to random occupation, and with center frequencies increasing with the number of Cd neighbors. Frequencies were adjusted to give a satisfactory agreement with the data. In the table, atomic configurations are identified by the number of Cd atoms attached to each Te first neighbor: for instance, 0001 denotes three Te sites with no Cd neighbors, and one Te site with a single Cd neighbor. 1* denotes the isolated Cd sites described above. Of the predicted resonance strengths, 80–90 % belong to the most prominent lines.

Shifts increasing with Cd neighbors is the trend for ^{199}Hg in these alloys,[5] and our fit provides a consistent description. Indeed, the 77-K shifts are almost entirely chemical shifts, as shown below, and these shifts for the two alloys are rather close for each configuration. Also, the $x=0.5$ peak value (2290 ppm reported earlier[5]) falls where one would expect, compared to that of the 4 and 5 neighbor configurations given in Table I, when one considers that the most probable configuration for $x=0.5$ is

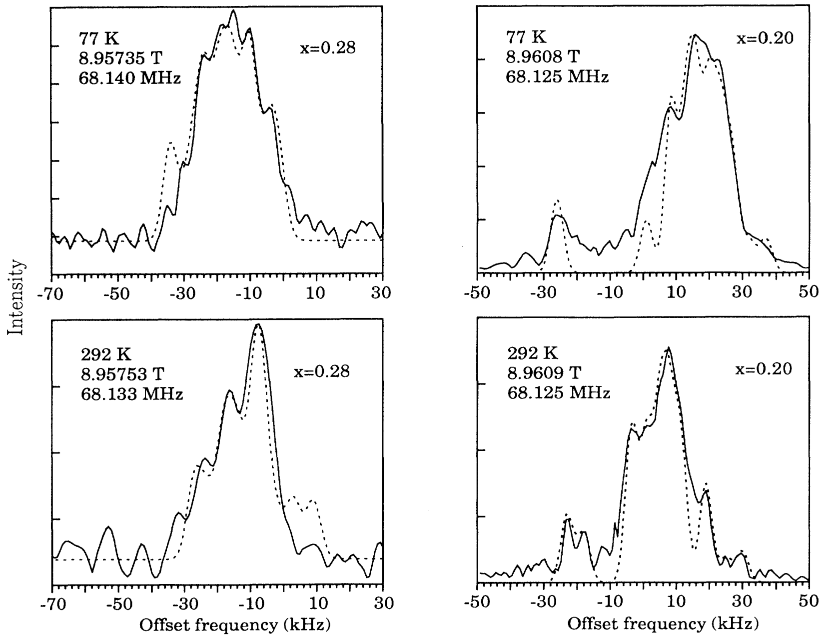

FIG. 1. ^{199}Hg NMR spectra for $Hg_{1-x}Cd_xTe$, at the indicated temperatures. Solid curves are the data, and dashed curves are the model, described in the text.

TABLE I. Resonance positions from model curves and temperature dependences for the two bulk alloys. Positions in ppm from bare ^{199}Hg, 7.590 12 MHz/T. Weights are for random occupation, and sites are identified according to the number of Cd per Te. Δ is the relative change from 77 to 300 K, in ppm. Positions for HgTe and $Hg_{0.5}Cd_{0.5}Te$ are from Willig *et al.* (Ref. 5).

	$x=0.20$				$x=0.28$			
Site	Weight (%)	77 K	292 K	Δ (ppm)	Weight (%)	77K	292 K	Δ (ppm)
0000	7	1260	1290	+30				
0001*[a]	4	1655	1370					
0001	17	1765	1580	−185	8	1745	1745	
0002/0011*[a]	13	1830	1640	−190	6	1835	1805	
0011	15	1875	1705	−170	13	1890	1875	−15
0012	12	1935	1740	−195	12	1960	1935	−25
0111	11	1985	1795	−190	13	2015	2010	−05
0112	9	2035	1905	−130	15	2090	2045	−45
1111					4	2140	2110	
1112	2	2105	1995	−110	6	2185	2185	
0122	2	2185	2070	−115	6	2225	2275	
c.m.		1798	1635	−163		1993	1970	−23
HgTe		450 ppm (4 K)						
$Hg_{0.5}Cd_{0.5}Te$		2290 ppm (4 K)						

[a] For a definition of the asterisk, see text.

6 neighbors. With these two constraints established, increasing the Hg shift with Cd neighbors and random-occupation weights, we find that the model curves are quite sensitive and strongly constrained by the data. The curves shown agree rather well with the data, and we believe that we have correctly identified the most prominent features in these lines.

In ^{125}Te NMR, a rather significant deviation from randomness has been identified for studies of similar alloys.[6,7,10] This may be a result of the powder sample and, indeed, a recent single-crystal study has not shown such deviations.[8] Very little deviation from random alloying is expected in equilibrium for these materials,[2] at least at bulk preparation temperatures, and our results are in good agreement.

IV. KNIGHT SHIFTS

A direct probe of the band edge is provided by the Knight shift, due to the spin susceptibility of charge carriers.[19] Fermi contact will dominate the Knight shift where charge carriers have *s* symmetry, with a considerably smaller contribution due to core polarization.[20] Spin-orbit interactions strongly affect the spin susceptibility of semiconductors, though, and this is the reason that the PbTe Knight shift is not proportional to spin polarization.[21–23] For direct-gap semiconductors, such as $Hg_{1-x}Cd_xTe$, this is easily accounted for via the effective *g* factor, or by utilizing band-edge parameters established by magneto-optical means.[24]

Knight shifts in semiconductors can be established by heavily doping the materials[25,26] and is an excellent means of probing the wave functions for charge-carrier states. In $Hg_{1-x}Cd_xTe$, heavy doping is a technical difficulty, and very uniform doping is required for this method. Hg, though, has large hyperfine coupling, and in narrow-gap $Hg_{1-x}Cd_xTe$ there are sufficient intrinsic carriers to give observable Knight shifts. Thus, we can measure these effects in low-doping device-quality crystals.

The Knight shift can be expressed as

$$K=n_e VP\frac{H_{\mathrm{HF}}}{H_0}\xi \ , \tag{1}$$

where n_e is the conduction electron density, P is their polarization, H_{HF} is the Fermi-contact hyperfine field, V is the primitive cell volume, H_0 is the applied field, and ξ is a parameter generally used to measure the *s*-orbital weight for conduction states and their distribution among sites. Only *s* electrons exhibit Fermi contact, and while electron carriers in CdTe are *s* type by symmetry, this symmetry is broken locally in the alloy, allowing a mixing of states. The nonstandard form (1) is needed because of nonlinear polarization in narrow-gap $Hg_{1-x}Cd_xTe$. The atomic hyperfine field for ^{199}Hg is 25.8 MG.[20] We have calculated the polarization for our three samples at room temperature and 77 K, using the formalism given by Weiler[24] (a spherical Kane model, using the parameters $E_p=19$ eV, and $\Delta=1$ eV). We included those electrons in the first three orbital-quantized levels, good to a few percent in all cases. We determined the polarization by integration of the Fermi function

$$n_i^{\pm} - \int_0^{\infty}\frac{k^2dk}{2\pi^2}\{\exp[E_i^{\pm}(k)-\mu]/kT+1\}^{-1} \ , \tag{2}$$

for the carrier density $n_i^{\pm}$ in each orbital quantized level, adjusting the chemical potential μ for the appropriate total carrier density. Carrier densities for our samples are listed in Table II; room-temperature intrinsic values are from Hansen, Schmidt, and Casselman.[27] Also given in Table II, with the resulting Knight shifts, are the experi-

TABLE II. Estimated and observed Knight shift, for the three samples studied, plus electron densities and band gaps. Band gaps are from Hansen, Schmidt, and Casselman (Ref. 27). The ΔK estimate, described in the text, is for 9 T. $\Delta K_{\text{c.m.}}$ is the center of mass observed shift, and ξ is the Hg s-orbital weight deduced from these shifts.

	77 K		292 K				
x	n (cm^{-3})	E_g (eV)	n (cm^{-3})	E_g (eV)	ΔK_{calc}	$\Delta K_{\text{c.m.}}$	ξ
0.20	1×10^{15}	0.158	3.5×10^{16}	0.084	−171	−163	0.95
0.22	1.35×10^{14}	0.182	2.2×10^{16}	0.115	−122	−100(10)	0.89(9)
0.28	$\approx1\times10^{14}$	0.264	6.5×10^{15}	0.211	−26	−23	0.92

mental results.

There is good agreement between the measured and calculated shift from 77 K to room temperature. Thus, the temperature dependence can be used to provide a measure of the Knight shifts. We note that holes are indeed present in the intrinsic regime as well as the electrons; these have much smaller effective g factors than the electrons, and so have been omitted from the analysis. Values for $x=0.22$ represent center-of-mass estimates directly from the spectra, not using the model outlined above for the smaller signals from this sample. On the other hand, values for the other two samples are obtained from Table I.

In all cases we find an average value of ξ in the range 0.90–0.95, with no dependence on x within the error of this experiment. These values can be compared to other measured values: 0.82 for ^{115}In in InSb,[26] and 0.70 for ^{113}Cd in CdTe.[25] Although HgTe and CdTe have nearly identical ionicities, it appears that conduction-edge states are more weighted to Hg than Cd. This is consistent with calculations[28] showing splitting of the lowest conduction band in this alloy into Hg- and Cd-like states, due to the lower Hg s energy. Furthermore, recall that HgTe has only p-symmetry carriers due to its inverted band edges. Such behavior in the alloy is inconsistent with the large shifts observed here, and we see that band-edge states change character immediately on the semiconducting side of the phase diagram.

Having carried out the structural analysis summarized in Table I, we now address local variations in the Knight shift. There are significant changes across the line, seen particularly in the $x=0.20$ sample, where the low-frequency "foot" clearly has a much smaller Knight shift than the rest of the line. This is the feature attributed to Hg sites with 12 second-neighbor Hg ions. These HgTe-like microclusters thus have conduction behavior similar to that of HgTe, in that we find little Hg s-orbital weight for this part of the line. (The HgTe resonance itself is well away from this position, so that macroscopic HgTe inclusions cannot be responsible for the resonance feature.)

This result—the lack of s-symmetry conduction electrons on HgTe-like microclusters—must be due to the influence of p-symmetry orbitals on those sites. In a diagonal-only treatment of alloy scattering,[29] an atomic potential difference of the order of the HgTe/CdTe band-gap difference is typically found. Diagonal scattering is sufficient to explain the ~40% drop in shift on the *high* side of the $x=0.20$ line, seen in Table I; regions associated with this part of the line are enhanced in Cd occupation, and so will tend to exclude conduction electrons. The response of the lower edge of the line can be understood if off-diagonal scattering between s and p orbitals is included. Indeed, core polarization[20] due to spin polarization in p orbitals on Hg in the HgTe-like microclusters may explain the small shift opposite in sign to the main line observed for these sites. Recently Kudrnovsky *et al.*[30] have indicated the importance of off-diagonal disorder in their calculations of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ electronic structures. From our results it appears that the effect on conduction electrons is most significant for smaller x compositions such as our $x=0.20$ sample, where regions of several atomic diameters containing no Cd atoms are statistically significant.

V. CHEMICAL SHIFTS

We not examine ^{199}Hg chemical shifts for these alloys, which are essentially the observed 77-K shifts for our samples, as was shown above. Large changes in the chemical shift with alloying imply significant changes in Hg local electronic structure; this was already noted by Willig *et al.*,[5] and is quite different from the behavior of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ (Ref. 9) and $\text{Ga}_x\text{In}_{1-x}\text{As}$ (Ref. 31) alloys. The shifts observed here are dominated by the term

$$\sigma=-\frac{\mu_0 e^2}{4\pi m^2}\langle r^{-3}\rangle\sum_{i,j}\frac{|\langle\psi_i|L_z|\psi_j\rangle|^2}{E_j-E_i}, \tag{3}$$

involving coupling of filled states $|\psi_i\rangle$ to unoccupied states $|\psi_j\rangle$. The L_z operator selects non-s-type states, giving the most important contributions from p-like upper valence-band states coupled to p-like middle conduction-band states—those involved in the strong E_1 and E_2 optical peaks.[32] In principle, d states may contribute, and shallow Hg 5d states do certainly participate significantly in the valence band.[33] However, (3) requires the coupling of orbits from the same shell, and the 5d content of conduction bands will be much less, giving little d contribution to the chemical shift. Thus, the large chemical shift increase with alloying must be due to an enhancement of the p character of Hg states, and in this we concur with Willig *et al.*[5]

The nature of this p-character enhancement is particularly relevant given the recent interest in charge-transfer processes in this alloy.[34–36] Such chemical shift changes are often associated with an ionicity change,[9] but this does not seem likely here since observed Cd chemical shifts exhibit the same trend as those of Hg,[5] and Te shifts show little change with alloying.[6] So, in an atomic-orbital picture, Hg *s* or *d* orbitals must lose charge to compensate for the *p*-orbital enhancement. Note that the upper valence states in HgTe already contain little *s* character; this is a symmetry requirement only along special lines in the zone (Δ, for instance), but apparently these states remain largely *p*-type in symmetry over the entire zone,[28] so that a loss in *s* character with alloying could not be a large effect. There is a much stronger mixing of *d* orbitals into these valence-band states, however,[35] and the large Hg chemical shift changes must be caused by a reduction in this mixing with alloying, giving therefore an enhancement in *p* character. It has indeed been proposed[35,36] that in the alloy the bonding charge near Hg associated with the *d* bands is enhanced. From the chemical shifts in the alloy it appears that this enhanced Hg *d* character of the buried *d* bands must be accompanied by a reduction of the Hg *d* character of the upper valence bands.

VI. CONCLUSIONS

We have performed ^{199}Hg NMR studies of $Hg_{1-x}Cd_xTe$ narrow-gap alloys, and we find that temperature-dependence studies do provide a sensitive measure of the Knight shift. From Knight-shift observations we found strong average Hg-site *s*-electron weights for the conduction band, somewhat larger than for Cd in CdTe. Furthermore, we have observed local difference in band-edge states, and found that mixing of *s* and *p* states at the band edge in the alloys can be important. Finally, we obtained ^{199}Hg chemical shifts for individual local configurations, and we have discussed the relationship of these shifts to charge transfer between orbitals in the alloys.

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