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Conduction-band formation in metal layers intercalated in TaS_2: Nuclear resonance of Sn, Hg, and Pb in TaS_2

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Metal layers of Sn, Hg, and Pb intercalated into TaS_2 have been studied by nuclear magnetic resonance. The completely intercalated layers in $Sn_{1.0}TaS_2$, $Hg_{1.0}TaS_2$, and $Pb_{1.0}TaS_2$ have fully metallic nuclear-resonance frequency shifts K with $K_{\parallel}$ and $K_{\perp}$ (parallel and perpendicular to normal to layers) $(0.69 \pm 0.02)\%$ and $(0.81 \pm 0.03)\%$ for Sn^{119} at 296 °K; $(1.66 \pm 0.01)\%$ and $(2.56 \pm 0.10)\%$ for Hg^{199} at 4.2 °K; and $(1.28 \pm 0.10)\%$ and $(1.54 \pm 0.05)\%$ for Pb^{207} at 296 °K. $Sn_{1/3}TaS_2$, which has an intercalated structure with one-third-filled Sr layers, yielded $K_{\parallel} = K_{\perp} = +(0.08 \pm 0.01)\%$ for Sn^{119} at 296 °K, suggesting a much smaller conduction-electron state density at the Fermi energy than in the fully filled layers. The Sn^{119} indirect nuclear-spin interaction through conduction electrons estimated from the measured T_2 values and calculated dipolar contribution was also weaker in $Sn_{1/3}TaS_2$ than in $Sn_{1.0}TaS_2$. A decomposition of the susceptibility components of the compounds is made. The Sn^{119} Mössbauer-effect splitting previously observed in $Sn_{1.0}TaS_2$ is shown to be produced by quadrupole effects. Interpretation of the conduction-band formation in terms of a Mott criterion is proposed.

Intercalation of atoms and molecules into layered materials produces an interesting new state of matter analogous in many ways to arrays of adsorbed surface layers. The transfer of charge on binding from intercalate layer to host can profoundly alter the host properties, while the intercalated layers themselves develop distinctive properties. In the present work, we investigate Sn-, Hg-, and Pb-intercalated TaS_2 by a study of the nuclear magnetic resonance of the intercalated metal atoms.

Although intercalation in TaS_2 causes little change in the structure of the TaS_2 layers, it does produce substantial changes in the susceptibility and superconducting transition temperature.[1] For all the metals studied, the large d-band paramagnetism of TaS_2 is reduced by intercalation. The superconducting transition temperature, T_c, on the other hand, may be raised or lowered. For full intercalation to compositions $Sn_{1.0}TaS_2$, $Hg_{1.0}TaS_2$, and $Pb_{1.0}TaS_2$, T_c is increased. But the partially intercalated compound $Sn_{1/3}TaS_2$ was not found to superconduct at all above 0.5 °K. The $\frac{1}{3}$ intercalated layer has a definite fractionally filled hexagonal structure and so does not consist of islands of fully intercalated regions.[1] The effective Sn radius (1.07 Å) and Mössbauer isomer shift in $Sn_{1/3}TaS_2$ corresponded to a Sn^{2+} charge state while the Sn radius (1.65 Å) in $SnTaS_2$ was much closer to that for neutral Sn^{0+}.[1] The Sn-Sn overlap in the $\frac{1}{3}$-filled layers is negligible ($r_{Sn-Sn} = 5.70$ Å), while in the filled layers the metal-metal distance (3.28 Å) approaches those (3.18 and 3.02 Å) in β-Sn, suggesting that the fully intercalated case superconductivity may be ascribable to conduction within the tin layers.[1] The Sn nuclear resonance might be expected to manifest the overlapping, neutral Sn atoms of the filled layers quite differently from the nonoverlapping, Sn^{2+} ions in the $Sn_{1/3}TaS_2$ compound.

Samples of powdered $Sn_{1/3}TaS_2$, $Sn_{1.0}TaS_2$, $Hg_{1.0}TaS_2$, and $Pb_{1.0}TaS_2$ were prepared as described in Ref. 1, passed through a 300-mesh screen and sealed under He gas for nuclear-resonance measurements, which were made with a Varian wideline NMR spectrometer and associated temperature-control and signal-averaging equipment. Frequency shifts were measured with respect to $PbSO_4$, $HgNO_3$, and LiCl reference solutions. [$\gamma(Sn^{119})/\gamma(Li^7) = 0.95914$ was used to obtain a Sn reference frequency.][2]

Tracings of the observed intercalate nuclear-absorption derivatives are shown in Fig. 1. (In no case was the Ta^{181} resonance observed, quadrupole broadening rendering it unobservable.) Sn^{119} in $Sn_{1/3}TaS_2$ showed a narrow line, 2-Oe wide between absorption-derivative peaks, with a small frequency shift [$+(0.08 \pm 0.01)\%$]. No temperature dependence of these parameters was observable between 11 and 500 °K. A much larger width and shift of Sn^{119} NMR was found in $Sn_{1.0}TaS_2$, where an asymmetric line shape apparently caused by anisotropic frequency shift was seen. Values of the frequency-shift components parallel and perpendicular to the layer normal (c axis) needed to fit the line at room temperature are $K_{\parallel} = +(0.69 \pm 0.02)\%$ and $K_{\perp} = +(0.81 \pm 0.02)\%$. These are similar in magnitude to the shifts in Sn metal, but with the opposite sign of anisotropy.[3] ($K_{\parallel} = +0.80\%$ and $K_{\perp} = +0.73\%$ in tin metal.) A decrease in the frequency-shift anisotropy was found on cooling to 11 °K. (See Table I.)

We are confident that the Sn^{119} NMR in these compounds arises from Sn in the layers, rather

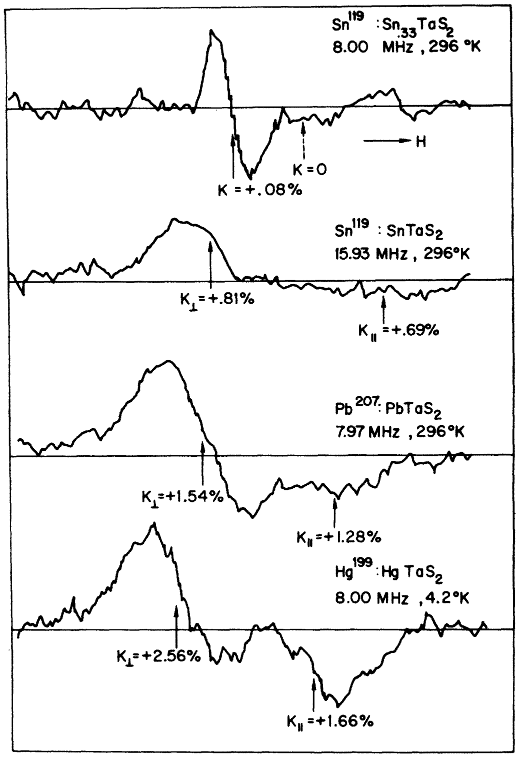

FIG. 1. Nuclear-resonance absorption derivatives for (a) Sn^{119} in $Sn_{1/3}TaS_2$, (b) Sn^{119} in $Sn_{1.0}TaS_2$, (c) Pb^{207} in $PbTaS_2$, and (d) Hg^{199} in $HgTaS_2$.

than in any possible Sn-metal agglomerations, since the frequency shift in $Sn_{1/3}TaS_2$ is much smaller than in Sn metal, and the shift anisotropy in $Sn_{1.0}TaS_2$ is of opposite sign from that in Sn metal. $K_\perp > K_\parallel$ in $Sn_{1.0}TaS_2$ is a result of a predominantly planar distribution of p-electron polarization, whereas the reverse inequality in Sn metal results from concentration of p magnetization along the c axis. The dipolar interaction is the primary anisotropic hyperfine interaction in each case. Coincidentally, these measurements resolve a paradox noted in the Sn^{119} Mössbauer-effect measurements in $Sn_{1.0}TaS_2$.[1] A two-peaked Mössbauer pattern was observed which was ascribable either to the presence of two inequivalent tin sites or to a large quadrupole interaction, the former having seemed more probable when the Mössbauer studies were made. The present NMR results show that the latter is now the most likely. Only one NMR line is seen, implying that there is but a single type of Sn site. Further, the frequency-shift anisotropy suggests a field gradient at the Sn site which would produce a quadrupolar splitting of the magnitude of the observed Mössbauer-effect line splitting. For an anisotropic charge distribution with k-independent wave functions, $K_\parallel - K_\perp \sim \frac{3}{2} \times \langle 3\cos^2\theta - 1\rangle \langle r^{-3}\rangle \chi_a$, while for one electron, the quadrupole interaction $(e^2qQ) \sim e^2\langle 3\cos^2\theta - 1\rangle\langle r^{-3}\rangle Q$. This yields $(e^2qQ)_{\text{cond el}} \sim 2e^2Q(K_\parallel - K_\perp)/3\chi_a$, where χ_a is the susceptibility per atom and $\langle r^{-3}\rangle$ is the mean inverse-cube radius of the p component of the wave function. Taking $\chi_{Sn} = 2\times10^{-5}$ emu/mole and $Q = 0.056$ gives $(e^2qQ)_{\text{cond el}} \sim 40$ MHz and a corresponding splitting of ~1 mm/sec, close to the observed Mössbauer-effect splitting of 1.14 mm/sec. While such estimates are very crude, they show that assignment of the Mössbauer-effect splitting to quadrupole interaction is reasonable.

We interpret the NMR to mean that for one-third-filled Sn layers, there is little density of Sn-conduction-electron states at the Fermi energy. Since, for a constant sp mixture, the frequency shift is proportional to $\eta_{Sn}(E_F)$, the state density is at most 0.1 that for Sn metal. Tin frequency shifts from supertransferred hyperfine interaction with the Ta d band will probably be 0.01 to 0.1 of those for Sn metal. This result is consistent with the Mössbauer-effect isomer-shift measurement showing a Sn^{2+} configuration in $Sn_{1/3}TaS_2$. The first two Sn conduction electrons are probably transferred to the TaS_2 d band, adding sufficient d electrons to that band to move the Fermi level above the large peak in the TaS_2 density of states, reducing the magnetic susceptibility from the TaS_2 value. The absence of superconductivity in $Sn_{1/3}TaS_2$ is presumably a result of insufficient state densities on either Sn or Ta sites to support superconductivity.

The magnitude of the $Sn_{1.0}TaS_2$ frequency shift,

TABLE I. Intercalate nuclear-resonance frequency shifts $K_\parallel$ and $K_\perp$ for magnetic fields parallel and perpendicular to normal to intercalate planes (c axis). Pure metal shifts are shown for comparison.

	T (°K)	$K_\parallel$ (%)	$K_\perp$ (%)
$Sn_{1/3}TaS_2$	296	+0.08 ± 0.01	+0.08 ± 0.01
	4.2	+0.08 ± 0.01	+0.08 ± 0.01
$Sn_{1.0}TaS_2$	296	+0.69 ± 0.02	+0.81 ± 0.02
	11	+0.75 ± 0.02	+0.81 ± 0.03
Sn^a	296	+0.80	+0.73
	4.2	+0.77	+0.69
$Hg_{1.0}TaS_2$	4.2	+1.66 ± 0.10	+2.56 ± 0.10
Hg^b	1.2	+2.28	+2.49
$Pb_{1.0}TaS_2$	296	+1.28 ± 0.10	+1.54 ± 0.05
Pb^c	296	+1.47	+1.47

[a] From Ref. 3.

[b] R. W. Weinert and R. T. Schumacher, Phys. Rev. 172, 711 (1968).

[c] L. H. Piette and H. E. Weaver, J. Chem. Phys. 28, 735 (1958).

on the other hand, requires a Sn conduction band for $SnTaS_2$ with similar Pauli paramagnetism to Sn metal. Since at most one electron per Ta atom is required for bonding of the Sn atoms to the TaS_2 layers (one electron being sufficient to fill the lowest Ta *d* band), there remain sufficient Sn *sp* electrons to populate the Sn conduction band.

Nuclear-resonance spin echoes were also observed from $Sn_{1/3}TaS_2$ and $Sn_{1.0}TaS_2$ at 1.5 and 4.2 °K using a pulsed spectrometer operating at 55 MHz. A Gaussian fit (e^{-t^2/T_2^2}) to the Sn^{119} spin-echo decay yielded a spin-spin relaxation time $T_2 = 540 \pm 100$ μsec in $Sn_{1/3}TaS_2$ at 1.5 °K and $T_2 = 90 \pm 10$ μsec in $Sn_{1.0}TaS_2$ at 1.5 °K. These imply homogeneous components of Sn^{119} second-moment linewidths of 0.26 and 1.52 G, respectively. A calculation of the dipolar second moment gave 0.26 G for both compounds, with Ta^{181} contributions dominating. The source of T_2 in $Sn_{1/3}TaS_2$ is thus dipolar, but the sixfold increase in the Sn^{119} relaxation rate in $Sn_{1.0}TaS_2$ relative to $Sn_{1/3}TaS_2$ must originate in some different interaction. The most likely source is an indirect Ruderman-Kittel interaction[4] through the Sn conduction band. Such a coupling is proportional to the Sn-site density of electron states at the Fermi energy and will be larger in $Sn_{1.0}TaS_2$. A similar value of T_2 (120 ± 30 μsec) was found in Sn metal, where indirect interactions also predominate.[4] Spin-lattice relaxation times of 48 and 2.4 msec were measured as well for $Sn_{1/3}TaS_2$ and $Sn_{1.0}TaS_2$ but were most likely impurity determined, since they were temperature independent between 1.5 and 4.2 °K and shorter than expected from the frequency shifts.

A partitioning of the susceptibility of the compounds into host and intercalate components is possible on the basis of the observed frequency shifts and bulk susceptibilities. Taking the *sp* admixtures and hyperfine constants to be the same as for tin metal and using atomic core values for the diamagnetism yields the decomposition shown in Table II. In both $Sn_{1/3}TaS_2$ and $Sn_{1.0}TaS_2$ the Ta paramagnetism is much smaller than in TaS_2. While the Sn-site paramagnetism reaches $+20\times10^{-6}$ emu/mole in $SnTaS_2$, the Ta-site paramagnetism has dropped to $+23\times10^{-6}$ emu/mole.

The resonances from Hg^{199} and Pb^{207} in $Hg_{1.0}TaS_2$ and $Pb_{1.0}TaS_2$ also showed large frequency shifts and asymmetric line shapes. The values of the frequency shifts are shown in Table I. The frequency-shift values, although of similar magnitude to those in mercury and lead metals, again show distinctively different anisotropy behavior from the pure metals. The $Pb_{1.0}TaS_2$ Pb^{209} shifts are anisotropic, while Pb metal, being cubic, has an isotropic shift. The Hg shift anisotropy in $Hg_{1.0}TaS_2$ has the same sign but greater magnitude than in Hg metal. Again, intercalated metal atoms form two-dimensional metallic sheets.[1] The drop in Ta-site susceptibility on Hg intercalation (Table II) is much smaller than on Sn intercalation, suggesting a smaller charge transfer and weaker Hg bonding. Thermogravimetric measurements determined that the Hg deintercalates between 200 and 300 °C, (rather than > 800 °C required for Sn), providing further evidence for weak Hg bonding. This deintercalation temperature is typical of weakly bonded organic molecules intercalated in TaS_2, where only small reductions in TaS_2 susceptibility are also observed.

The process by which conduction bands are formed in the intercalated layers probably involves the satisfaction of a Mott criterion for conductivity.[5] For one-third-filled Sn layers, the Coulomb energy gained by localizing states should exceed the width of the intercalate bands, both be-

TABLE II. Susceptibility components of TaS_2, $Sn_{1/3}TaS_2$, $Sn_{1.0}TaS_2$, and $Hg_{1.0}TaS_2$. The diamagnetism values are the estimated core contributions, the Sn paramagnetism values are calculated from

$$\chi_{\mathrm{para}}^{(\mathrm{Sn:Sn}_x\mathrm{TaS}_2)} = \frac{K(\mathrm{Sn}^{119}\colon \mathrm{Sn}_x\mathrm{TaS}_2)}{K(\mathrm{Sn}^{119}\colon \mathrm{Sn})}\,\chi_{\mathrm{para}}(\mathrm{Sn}),$$

and the TaS_2 paramagnetic susceptibility is obtained by subtraction of the other components from the total observed susceptibility. All values are in units 10^{-6} emu/mole.

	χ_{dia} (Sn, Hg)	χ_{para} (Sn, Hg)	χ_{dia} (TaS_2)	χ_{para} (TaS_2)	$\chi_{\mathrm{obs}}^{\mathrm{tot}}$ [a]
TaS_2	···	···	−56	+194	+138
$Sn_{1/3}TaS_2$	−5.3	+0.7	−56	+54	−7
$Sn_{1.0}TaS_2$	−16	+20	−56	+23	−29
Sn	−16	+19	···	···	+3
$Hg_{1.0}TaS_2$	−83	+25	−56	+148	+34
Hg	−83	+27	···	···	−56

[a] Data in part from Ref. 1.

cause Sn^{2+} states formed by intercalation charge transfer will be electrostatically stable and because the large Sn-Sn separation will not broaden the Sn conduction bands. Consequently the Mott conductivity criterion that the bandwidth exceed the Coulomb localization energy is not met for $Sn_{1/3}$ intercalation, and the tin bands do not support conductivity. For full intercalation though, there is insufficient ionization to deplete an intercalate band, making charge fluctuations energetically more favorable. The closer metal-metal spacings will produce a wider band so that conductivity is to be expected within the layer. Whether the conductivity is dominated by intercalate-to-intercalate paths or intercalate-to-tantalum paths is not resolved by the measurements. Studies of the anisotropy of resistivity would be interesting in this regard.

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