PHYSICAL REVIEW B VOLUME 37, NUMBER 6 15 FEBRUARY 1988-II

Brief Reports

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Mössbauer studies of the 6.2-keV γ rays of ^{181}Ta in $2H$-Li$_x$TaS$_2$ ($0 \le x \le 0.95$)

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(Received 25 June 1987; revised manuscript received 22 September 1987)

High-resolution Mössbauer resonance of the 6.2-keV γ rays of ^{181}Ta has been observed in $2H$-Li$_x$TaS$_2$ ($0 \le x \le 0.95$). The isomer-shift (IS) results have been found to be proportional to the Li concentration and in turn to the charge transfer. This IS increases from 72.3 mm/s for $x=0$ to an IS of 100 mm/s for $x=0.95$. The IS results reflect the change of the electronic configuration of Ta from Ta^{4+}($5d^1$) toward Ta^{3+}($5d^2$) and an increase in ionicity as the lithium content increases from 0 to 0.95. The electric quadrupole splitting as a function of Li content indicates the observation of a phase change.

Interest in layered compounds especially the transition-metal dichalcogenides[1] has grown very rapidly in the last 15 years. This interest stems from the discovery of charge-density-wave phenomena[2,3] and from a large variety of intercalation compounds[4] some of which may have potential technological applications.[5] The recognition that the intercalation process can radically alter the basic properties of the layer dichalcogenides has prompted the need to establish a fundamental understanding of the physics associated with these rather remarkable solid-state systems.[1] Intercalation of the layer structure transition-metal disulfides is possible for a wide variety of electron donor species including alkali metals.[4] Although it is commonly accepted that for a system such as the $2H$-Li$_x$TaS$_2$ ($0 \le x \le 1$) system there is a transfer of electrons from the intercalant Li atoms to the Ta $5d^1$ band, but direct experimental evidence is lacking.[6,7] The 6.2-keV γ rays of ^{181}Ta Mössbauer effect (ME) are especially suited for this application because, of all the Mössbauer isotopes, ^{181}Ta has the highest sensitivity to small changes in the electron density at the nucleus.[8] We report here ^{181}Ta ME measurements in Li$_x$TaS$_2$ which represent a unique method to study the electronic configuration of Ta atoms in layer compounds. These are the first such measurements in Li$_x$TaS$_2$. The ME resonance allows us to deduce the charge transfer directly in terms of isomer shift (IS) measurements. The ME IS results show that the electronic configuration of Ta depends on the Li concentration. The IS results for the first time have been found to be proportional to the charge transfer from the donor Li to the host $2H$-TaS$_2$ over a wide range of intercalant concentration.

Each layer of $2H$-TaS$_2$ is a sandwich of metal Ta atoms in sites of trigonal prismatic symmetry between planes of closed packed chalcogen S atoms. The bonds within the layers are strong and primarily covalent, but between adjacent S layers are weak, primarily Van der Waals.[1,4] In Li$_x$TaS$_2$ the Li ions occupy octahedral sites between the TaS$_2$ layers.[5,6]

The ^{181}Ta Mössbauer spectra were obtained in transmission geometry with a conventional sinusoidal electromechanical drive. The source was made by diffusion of ^{181}W activity into a high-purity single crystal of tungsten under ultra-high vacuum conditions. Each absorber was a single unstrained crystal platelet of Li$_x$TaS$_2$ with the c axis parallel to the γ rays. The dimensions of the single crystal were $5 \times 4 \times 0.006$ mm^3. The source and absorber were mounted in a common vacuum chamber to eliminate acoustical disturbances[9] and prevent oxidation of the sample. The 6.2-keV γ rays were detected with a proportional counter filled with an argon-krypton CO$_2$ mixture. Single crystals of $2H$-TaS$_2$ were prepared from powder of the respective materials by iodine transport. The Li$_x$TaS$_2$ compounds were prepared by the reaction of precleaved single crystals of $2H$-TaS$_2$ with n-butylithium at 50 °C followed by annealing at 300–500 °C. X-ray diffraction confirmed the presence of the $2H$ phase. The increases in the c crystallographic axis obtained are in agreement with those reported in the literature.[1] The Li concentration was determined by atomic emission spectroscopy. The room-temperature Mössbauer spectra of $2H$-Li$_x$TaS$_2$ crystals as a function of lithium concentration (from

$x = 0$ to 0.95) are shown in Fig. 1.

The ^{181}Ta spectrum for $x = 0$ for 2*H*-TaS_2 is characteristic of a hyperfine pattern resulting from electric quadrupole interaction.[9] The spectrum shows two resonance peaks indicating that all the Ta are in equivalent crystallographic sites. Each peak is a superposition of two nuclear transitions. Some spectra for $x > 0$ are broadened and show the existence of two or more sites. When a line broadening is observed it is usually due to concentration gradients in the sample. These spectra indicate that the concentration of Li between the layers is not perfectly uniform, but rather has a concentration distribution of about 5%. Annealing at 400–500 °C in vacuum for four to six days produced no noticeable change in the Mössbauer spectra. This inhomogeneity is not observed by x-ray diffraction. The spectrum for $x = 0.74$ Li can be decomposed into two subspectra similar to the one without Li. The spectrum indicates that there are two different concentrations of Li of approximately 5% apart. The IS is slightly different between the two concentrations of Li, but they have about the same electric quadrupole interaction. This shows the high sensitivity of the IS of the 6.2 keV ^{181}Ta Mössbauer effect. The spectrum with $x = 0.95$ Li could be fit with three sites or with a distribution of Ta sites as shown in Fig. 1. The observation of two more inequivalent Ta sites indicates that the residence time for the intercalant is large compared to the precession period $\gg 10^{-8}$ s, or that the Li concentration is not uniform between the layers. The absorption spectrum has been fitted by least squares using the well-known dispersion modified Lorentzian lines.[10] A value of $2\xi = -0.30$ (Ref. 8) for the dispersion term and a fixed quadrupole ratio $Q_{\frac{9}{2}}/Q_{\frac{7}{2}} = 1.1315$ (Ref. 11) were used in the nonlinear least-squares computer fits. The measured spectra are in very good agreement with the assumption of an axially symmetric electric field gradient, which is expected from the trigonal prismatic structure of the material.

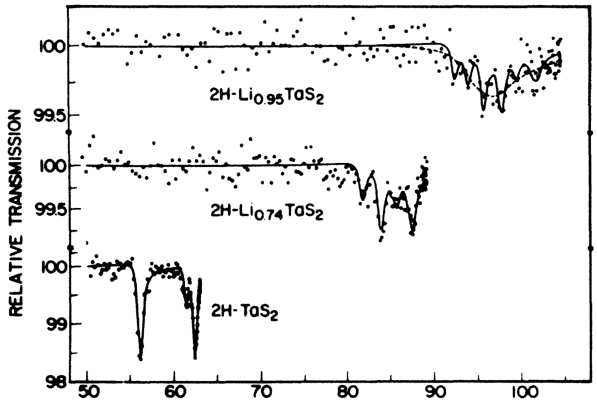

FIG. 1. Room-temperature Mössbauer absorption spectra of ^{181} Ta in 2*H*-Li_xTaS_2 for $x = 0$ to 0.95. The source was ^{181}W in tungsten metal and the absorbers were an unstrained single-crystal *c* platelet for each concentration. The solid lines are the result of least-squares fits of superposition of dispersion modified Lorentzians to the data. The dashed curve for $x = 0.95$ shows the distribution of sites.

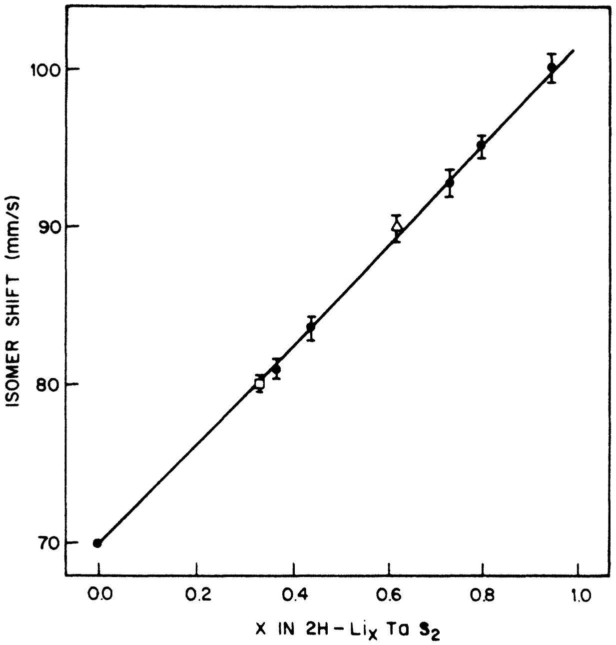

FIG. 2. Isomer shifts of the 6.2-keV γ rays of ^{181}Ta in 2*H*-Li_xTaS_2 for $x = 0$ to 0.95 expressed relative to Ta metal at 296 K [●, Li; □, $Na_{1/3}(H_2O)_2TaS_2$; △, $Ag_{0.62}TaS_2$].

The isomer shift is a measure of the *s*-electronic charge density at the nucleus and is affected by the valence state of the Ta atoms. The IS as a function of Li concentration is shown in Fig. 2. An increase in IS from 70.26 for $x = 0$ (no Li) to 100 mm/s for $x = 0.95$ (almost fully lithiated) has been observed. The IS has been found to be proportional to the Li concentration, and in turn to the charge transfer. Assuming that Li is essentially ionic and a complete charge transfer to the Ta site occurs, then an IS change of ~30 mm/s per e^- has been derived.

It is interesting to note that the IS of Na intercalated hydrated sample $Na_{1/3}(H_2O)_2TaS_2$ (Ref. 12) and Ag in-

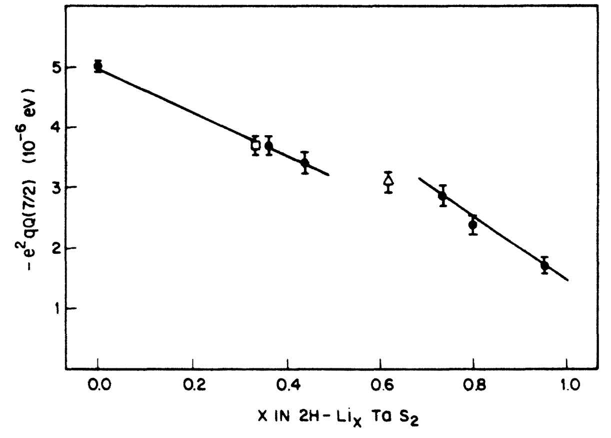

FIG. 3. Electric quadrupole interaction $-e^2qQ_{\frac{7}{2}}$ in 2*H*-Li_xTaS_2 for $x = 0$ to 0.95 [□, $Na_{1/3}(H_2O)_2TaS_2$; △, $Ag_{0.62}TaS_2$].

tercalated compound $Ag_{0.62}TaS_2$ (Ref. 13) fall on the same curve with Li_xTaS_2 (Fig. 2). These results indicate that the IS is independent of the donor species as long as the donor behaves as a monovalent ion. Therefore, the electron charge transfer from the donor to the acceptor is independent of the intercalant. An important conclusion is that as long as we are dealing with ionic monovalent intercalates we can use the measured IS and deduce the charge transfer from Fig. 2.

The electric quadrupole splitting (QS) $-e^2qQ\frac{7}{2}$ as a function of Li concentration is given in Fig. 3. The QS as a function of LI content is not a parabolic function as proposed by time differential perturbed angular correlations (TDPAC) measurements.[14] The above results indicate that TDPAC measurements are not accurate enough to measure the charge transfer. The QS initially decreases smoothly with the Li content from a QS of -5.01×10^6 eV for $x=0$ to a QS of -1.7×10^6 eV for $Li_{0.95}TaS_2$, and develops a break around $x\approx0.5$ indicating a phase change.

The types of possible phase transitions which seem likely in the $2H$-Li_xTaS_2 system include a metal to semiconductor transition, ordering of lithium, staging, and induced charge density waves. $2H$-TaS_2 is metallic and band-structure calculations[15,16] indicate the presence of a half-filled 1-eV wide two electron d_z^2 conduction band. At $Li_{1.0}TaS_2$ this band will be filled and semiconducting behavior would be expected. Our samples are still metallic[17] at $x=0.9$, excluding a metal insulator transition at $0.4<x<0.7$. Deviations from ideal electrochemical data in $2H$-Li_xTaS_2 have been observed and ascribed to stage-two ordering at $0.11<x<0.16$ and lithium ordering at $x=0.33$ and $x=0.66$.[18] We believe that some type of lithium ordering is responsible for the phase change observed by the Ta Mössbauer spectra even though it is not observed by x-ray diffraction. We believed this data shows that such ordering is more complicated than indicated by electrochemical data.

This work has shown that ^{181}Ta Mössbauer resonance is a very sensitive tool to study the electronic charge transfer and local structure in Ta dichalcogenides. In particular, the charge transfer is independent on the monovalent donors (Li^+, Na^+, or Ag^+) and that the IS in Li_xTaS_2 is proportional to the Li concentration. The increase in IS from 70.28 mm/s for $x=0$ (no Li) to an IS of 100 mm/s for $x=0.95$ (almost fully lithiated) reflects the change of the electronic configuration of the host from $Ta^{4+}(5d^1)$ toward $Ta^{3+}(5d^2)$ and an increase in ionicity as the lithium content increases from 0 to 0.95. The QS initially decreases smoothly with Li content but develops a break around $x=0.5$ indicating a phase change. Finally, a value of 30 mm/s per e^- is the most reliable lower bound calibration for an IS-valence correlation.

We thank J. V. Waszczak for the $2H$-TaS_2 crystals and L. F. Mattheiss and P. Littlewood for helpful discussions.

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