JOURNAL OF SOLID STATE CHEMISTRY **24**, 219–225 (1978)

Incoherent Neutron Spectra of H_xTaS_2, a Nonstoichiometric Covalent Tantalum Hydrosulfide

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Received August 3, 1977; in revised form October 5, 1977

Inelastic neutron spectra show the presence of a fundamental hydrogen vibration at 712 and 744 cm^{-1} in $H_{0.1}TaS_2$ and $H_{0.5}TaS_2$, respectively. This permits the structural deduction that H_xTaS_2 is a nonstoichiometric covalent metal hydrosulfide. In $H_{0.5}TaS_2$ another low-intensity band in the spectrum may be interpreted as suggesting the presence of a small concentration of SH^- anions. An X-ray diffraction pattern taken after the neutron experiments reveals partial decomposition to TaS_2 and the presence of satellites to the (00*l*) reflections show the decomposition to be a process involving considerable long-range order.

Introduction

Intercalation compounds of the layered transition metal dichalcogenides (MX_2, X = S, Se, Te) have been much studied in recent years (*1*). The intercalated materials, although varied in nature, are basically all capable of at least partial electron donation to the MX_2 conduction band, and systems with alkali metals (*1*), transition metals (*1*), hydrated metal ions (*3*), and organic bases (*1*) as the guest species have all been subject to wide-ranging investigation, often with regard to physical properties such as electronic conductivity, optical properties, fast alkali metal ion transport, and superconducting phenomena.

Although hydrogen gas does not react directly with tantalum sulfide (*3*), except to cause decomposition above 400°C, a hydrogen tantalum sulfide may be formed by electrolysis of 2H–TaS_2 suspended in sulfuric acid (*4*). A range of stoichiometry of H_xTaS_2 with $0 < x < 0.87$ was found where x was estimated coulometrically. The hydrogen did not appear to be accompanied by water to any significant degree. In the light of the rapid preparation of the compound at room temperature, and the high mobilities found, for example, for lithium in stoichiometric TiS_2 (*5*) and ammonia in tantalum disulfide (*6*), interest attaches to hydrogen tantalum sulfide as a possible fast proton-conducting material.

Although the TaS_2 lattice is retained on intercalation, the detailed crystal structure is not known and it has been unclear whether H_xTaS_2 should be regarded as analogous to the alkali metal intercalates or as a covalent tantalum hydrosulfide of variable stoichiometry. The latter possibility would let H_xTaS_2 appear to be a novel chemical species as, in contrast to the numerous metal hydroxides and oxyhydroxides, the only well-established inorganic hydrosulfides are the ionic alkali metal salts containing discrete SH^- ions. On the other hand it seems unlikely that hydrogen would occupy a similar crystallographic

0022-4596/78/0242-0219$02.00/0

Printed in Great Britain

position to intercalated metal atoms which are generally found in sixfold coordination symmetrically placed between the sulfur layers. Moreover, at low hydrogen concentrations no increase in layer separation relative to 2H–TaS_2 was observed (*4*) and an increase of only ~0.2 Å was found at the highest hydrogen concentrations.

Although sensitive to air and moisture, H_xTaS_2 in the composition range $0 < x < 0.6$ is reported to be thermally stable at room temperature. The TaS_2 band structure is perturbed on intercalation as is the case for other intercalates, and this is reflected, for example, by changes in color (*4*) and structure (*4*) when the hydrogen content is very high. To understand and predict the physical properties of H_xTaS_2, we need information on the location of the hydrogen and the nature of its bonding to the disulfide lattice. If each proton is covalently bonded to one sulfur atom then the proton mobility will probably be low, because of the considerable bond-breaking energy barrier to be overcome prior to diffusion. Characteristic sulfur–hydrogen stretching and bending vibrations may be observable and H_xTaS_2 should be regarded as a nonstoichiometric phase rather than an intercalate. In this case it would be analogous to oxides such as hydrogen β-alumina (*7*) the hydrogen tungsten bronzes (*8*) and $H_{0.34}MoO_3$ (*9–11*). If, however, the hydrogen is shared between more than one sulfur atom, the vibrational frequencies will be lower than in the first case and the proton mobility may be much higher. The vibration spectrum is therefore a very useful indicator of the nature of the proton binding, but in metallically conducting systems such as H_xTaS_2 it cannot readily be observed by conventional optical techniques.

We have shown previously, in H_xWO_3 (*12*) and TaS_2–$(\text{pyridine})_{1/2}$ (*13*) for example, that incoherent neutron spectroscopy can supply such information and we present here spectra of (nominally) $H_{0.1}TaS_2$ and $H_{0.5}TaS_2$ taken using a beryllium filter spectrometer. We chose two quite different compositions to ascertain whether there was any significant change in the hydrogen binding as the hydrogen content is varied. The neutron spectra were measured at 80°K where an $H_{0.1}TaS_2$ sample would be close to or in the region where the charge density wave driven lattice distortion is still occurring (*4*), whereas for $H_{0.5}TaS_2$ this distortion is almost certainly suppressed.

Experimental

The materials were prepared by cathodic reduction of 2H–TaS_2 pressed powder electrodes as described by Murphy *et al.* (*4*) with the composition controlled by galvanostatic methods. The samples were stored for 3 days at room temperature under inert gas before being transferred under nitrogen into silica tubes for the high-energy-transfer spectroscopic measurements which were performed at 80°K using the beryllium filter spectrometer at the I.L.L. Grenoble. The data were corrected for instrumental effects in the usual way (*14*). Lower-energy spectra were measured a few days later for $H_{0.5}TaS_2$ at room temperature with the 6H time-of-flight spectrometer at AERE Harwell. The transfer of the materials was accompanied by a strong odor of H_2S, and X-ray reexamination of $H_{0.5}TaS_2$ a week after the final experiment showed that partial decomposition had occurred. The compositions quoted are therefore only nominal, but neither any uncertainty in the stoichiometry nor the possibility of partial decomposition affect the discussion in any material way. The diffraction pattern observed is discussed below.

Results and Discussions

Figure 1 shows the beryllium filter spectra of nominally $H_{0.1}TaS_2$ (a) and $H_{0.5}TaS_2$ (b). From the intensities and positions of the bands observed it would appear that for $H_{0.5}TaS_2$ we are observing a fundamental excitation and its first three harmonics, and the fundamental and one harmonic for $H_{0.1}TaS_2$. As there appears

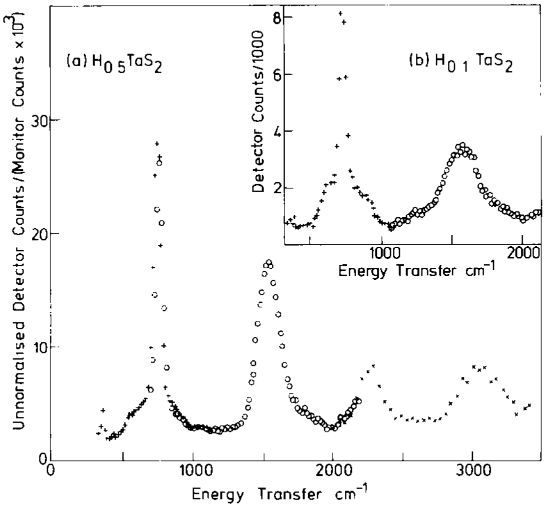

FIG. 1. Inelastic neutron spectra for (a) $H_{0.1}TaS_2$ and (b) $H_{0.5}TaS_2$.

to be no previous preparation of a covalent inorganic hydrosulfide we are unable to assign our spectra by analogy. However, the spectra of organic hydrosulfides are well documented and the range of the C–S–H deformation vibrations is 805 → 905 cm^{-1} (*15*). By comparison with this we assign our vibration at 744 cm^{-1} to a Ta–S–H deformation. We consider below all the other possible structural models for our material, and we can exclude each of them in turn. We conclude therefore that H_xTaS_2 is a nonstoichiometric, metallic, covalent hydrosulfide analogous to the metallic covalent hydroxides of tungsten (*8*, *11*) and molybdenum (*9*, *10*). A neutron diffraction study to locate the proton positions is presently underway.

The other possible structural models involve either the pairing of protons in coordinated H_2S groups, the presence of interlayer hydrogen molecules or the presence of weakly coordinated interlayer hydrogen atoms or ions. The first can be ruled out by the absence of scattering in the region of 1214 cm^{-1} (*16*), the frequency of the deformation vibration of H_2S. Similarly the latter two models can also be eliminated by the absence of additional scattering at energies less than 744 cm^{-1} of sufficient intensity to be associated with the translations or rotations of H_2 molecules or with other fundamentals of an interstitial atom or ion in what must necessarily be an anisotropic site.

The relative intensities of the fundamental and the harmonics may be analysed to give an estimate of the isotropic Debye–Waller factor. From the scattering law for an anisotropic simple harmonic oscillator (*17*) the relative intensities of a fundamental and its harmonics can be predicted. When the hydrogen atoms are also sensitive to the motion of their environment the simple theory no longer applies, but as we have shown before (*12*) this case can be treated empirically by replacing the exact exponential term in the scattering law with a measured Debye–Waller factor and by neglecting the average over all orientations of the sample with respect to the momentum transfer. This neglect of the orientation average does not have a very serious effect upon the relative values of $S(\mathbf{Q},\omega)$ at different values of ω. Writing the scattering law for neutron energy loss as (*12*):

$$S(\mathbf{Q}, \Omega) = \exp\left(\frac{-\hbar Q^2}{2m\omega_0}\,\frac{\coth\hbar\omega_0}{2kT}\right)\frac{1}{n!}\left(\frac{\hbar Q^2}{2m\omega_0}\right)^n \tag{1}$$

which is valid at the temperatures and energy transfers of our experiment, we can substitute for the first term an experimentally measured Debye–Waller factor to give

$$S(\mathbf{Q}, \omega) = e^{-Q^2C}\,\frac{1}{n!}\left(\frac{\hbar Q^2}{2m\omega_0}\right)^n, \tag{2}$$

where n is the number of excitations, Q is the momentum transfer, C is a constant, and ω_0 is the frequency of the fundamental. From this expression we find that $\log_e$ [(intensity of the nth harmonic)/$(1/n!)(\hbar Q^2/2m\omega_0)^n$] should be linearly dependent upon Q^2 and Fig. 2 shows that this is indeed the case. This justifies our assumption that the higher-energy bands are harmonics, and indicates that the above expression can be of general utility in calculating the intensities of higher harmonics in

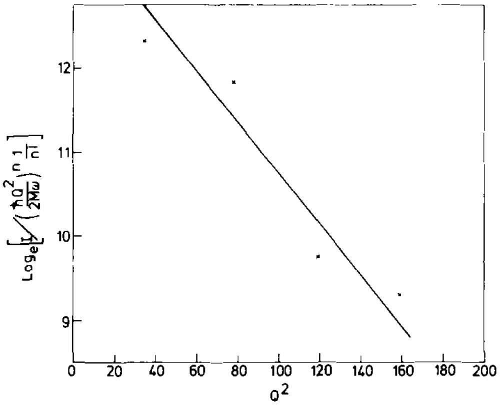

FIG. 2. Relationship of $\log_e$ [(peak intensities/$(1/n!)(\hbar Q^2/2m\omega_0)^n$)] to Q^2.

situations where they overlap higher-energy fundamental vibrations of interest. The intensities, which were measured in arbitrary units, were obtained by integrating over the whole of the area of each band in Fig. 1.

Calculations of the multiple scattering contributions to the spectra were performed by Dr. M. W. Johnson with the program DISCUS (*18*). Although these were appreciable, ~25%, their values as a proportion of the measured intensity did not change between the different harmonics. Their neglect in this case would not therefore have influenced the analysis. Details of relevance to the calculation were the sample transmissions which were 85% at $E_0 = 93$ meV, and the fact that the samples were in transmission geometry at 45° to the incident beam.

The slope C of the line of Fig. 2 corresponds to an isotropic temperature factor $B = 24\pi^2 C$, of 7.2 Å^2 and a frequency ω_0 in the exponential expression,

$$\exp\left\{\frac{-\hbar Q^2}{2m\omega_0} \coth \frac{\hbar\omega_0}{2kT}\right\},$$

taken from Eq. (1), of 544 cm^{-1}. For a perfect harmonic oscillator this frequency should of course be 744 cm^{-1}, the frequency of our measured fundamental.

We note the absence of any detectable scattering from the hydrogen–sulfur stretching vibration. Again by analogy with other hydrosulfides we should expect this vibration to fall in the 2500- to 2700-cm^{-1} region in the gap between the scattering from the third and fourth harmonics of the deformation vibration. Reference to Fig. 1 shows that there is no significant scattering here above the background level. We can explain this phenomenon using the simple harmonic oscillator theory of Ref. 16. This shows that the intensity of the stretching vibration will be about one-third of the intensity of the harmonics of the deformation vibration in the same region of the spectrum, and so may be hard to distinguish from them.

An additional feature in the beryllium filter spectra is the appearance of a broad band of scattering beneath the central peak for both $H_{0.1}TaS_2$ and $H_{0.5}TaS_2$. We have already eliminated the possibility that this could be due to hydrogen molecules with their associated rotational broadening, and this is confirmed by the time-of-flight measurements at lower energies conducted at room temperature which show no broadening of the energy distribution of elastically scattered neutrons. Translational diffusion of hydrogen atoms, unlikely to be taking place at a rate measurable by neutron scattering at 80°K, is not a phenomenon which could give rise to the narrow central peak superimposed upon a broader background that was observed.

We can suggest two possible causes of this effect. Either we are observing combination and difference bands involving the fundamental and a vibration of the TaS_2 lattice, or scattering from protons in a range of geometries. We feel the latter explanation is to be preferred, for it is impossible to explain the relative intensities of the possible combination and difference bands using our approximation to the simple harmonic oscillator theory. The ratio of the intensities of the combination and difference bands of two harmonic vibrations should be (*17*)

$$\frac{I_C}{I_D} = \exp(-(Q_C^2 - Q_D^2)C) \times \exp\left(\frac{\hbar(\omega_C - \omega_D)}{2kT}\right)\frac{Q_C^4}{Q_D^4}$$

and if we use the same Debye–Waller factor for these bands as was derived above then the intensity ratio for scattering at 20 meV greater and less than the fundamental is

$$I_C/I_D = 31:1.$$

We would also expect a ratio of similar order to obtain for multiphonon scattering. This is in total disagreement with the approximately equal ratio observed. Further, if these were combination and difference bands we would expect the discontinuities in the intensity variation to appear at equal separations from the central peak for both bands and for both samples. This is not the case, as is shown in Table I. The differences between the spectra of the two samples are most marked on the low-energy side. Finally, although we agree with a reviewer in his suggestion that our observed bandwidths may be influenced by hydrogen–hydrogen interactions and consequent phonon dispersion, we feel that the absence of such effects in the neutron spectra of similar hydrogen containing metallic chalcogenides (*10*, *12*) allows us to rule out that possibility. It is worth commenting that in these other cases well-formed crystalline samples were investigated.

Thus in addition to the majority of protons bound as Ta–S–H, which give rise to the sharp central maximum in the scattering and which sit in apparently identical sites, we think there is also a fraction which appear to occupy a distribution of different sites and which cause the broad band in the scattering. It is not clear whether these other sites result from stacking disorder in the TaS_2 lattice, from impurities introduced during the preparation process or from partial decomposition.

The X-ray diffraction pattern from the sample of $H_{0.5}TaS_2$ taken after the neutron diffraction experiments indicates partial decomposition. We cannot tell how much of this change had occurred at the time of the beryllium filter measurements, but at least a part of the reaction took place when the sample was exposed to air to run the diffraction pattern; the considerable odor of hydrogen sulfide indicated ongoing attack by atmospheric moisture. The pattern rather interestingly reveals that the decomposition is a process involving long-range interactions. The intensity distribution around all the observable $(00l)$ peaks is similar to that shown for the (004) peaks in Fig. 3.

In this figure the two most intense peaks can be indexed as the (004) reflections of TaS_2 and H_xTaS_2. Lattice constants determined from an analysis of the complete pattern were $a = 3.31$ Å, $c = 12.14$ Å, and $a = 3.31$ Å, $c = 12.29$ Å, respectively. With two formula units per cell these values correspond to an increase in layer spacing due to the hydrogen of only 0.07 Å, in fair agreement with the earlier observations (*4*).

The observation of satellite peaks A, B, and C can be explained by a modulation of the TaS_2 lattice in both unit cell parameter and scattering factor, resulting from a decomposition of H_xTaS_2 which is incomplete but highly correlated from layer to layer (*19*).

TABLE I

Sample	Low-energy discontinuity and separation from central peak (cm^{-1})	Central peak (cm^{-1})	High-energy discontinuity and separation from central peak
$H_{0.1}TaS_2$	600 (−112)	712	904 (+192 cm^{-1})
$H_{0.5}TaS_2$	522 (−222)	744	Continuous

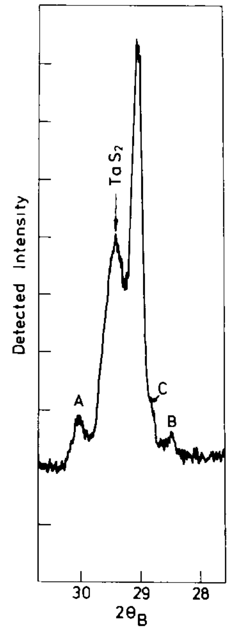

FIG. 3. X-Ray diffraction pattern of $H_{0.5}TaS_2$ taken after the neutron experiments in the region of the (004) peak.

A, B, and C can be indexed as the $(0\,0\,4 \pm (3/A)$ and $(0\,0\,4 + (5/A)$ satellites with A, which is the period of modulation of the lattice parameter, equal to 450 Å. The TaS_2 peaks all have greater linewidths than those of the H_xTaS_2, which is probably due to stacking disorder induced on decomposition.

It is important to note that any partial decomposition of the $H_{0.5}TaS_2$ and the consequent presence of TaS_2 at the time of the neutron-scattering experiments will not affect the analysis because of the very low scattering cross section of the dehydrogenated material.

Figure 4 shows the differential scattering cross section from the time-of-flight experiment (a), and the data (measured at lower frequencies) converted to the amplitude weighted density of states (b) so that the intensities can be directly compared with those of Fig. 1. It can be seen that in addition to the scattering near to 750 cm^{-1} there is also scattering at 300 cm^{-1} with an intensity in the scattering law amounting to 2% of the intensity at 744 cm^{-1}. The narrow bandwidth of this excitation means that it is unlikely to be scattering from the acoustic density of states of the TaS_2 and the optical excitations in this material will occur at higher frequencies (*20*). We are led to speculate that this excitation originates from another source which might be a low concentration of HS^- anions accounting for about 2% of the total hydrogen content of the material. Such a group would give rise to a librational (*21*) excitation in the neutron

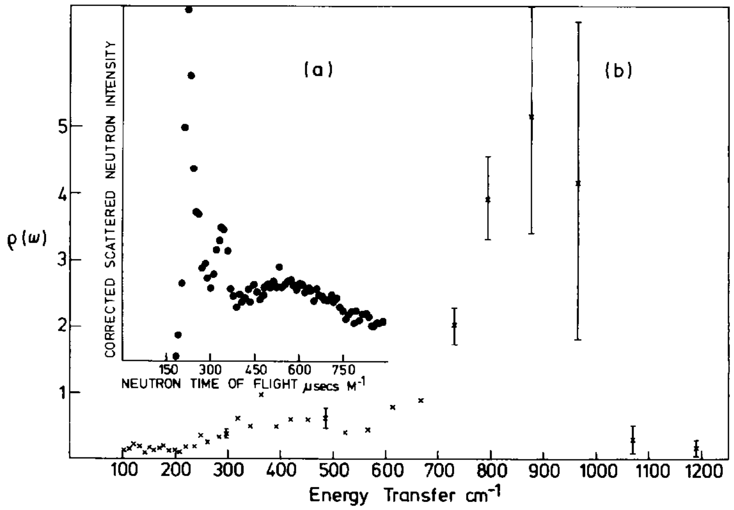

FIG. 4. Differential scattering cross section and amplitude-weighted density of states at lower energies for $H_{0.5}TaS_2$.

spectrum accompanied by much weaker translational excitations which we would not be able to observe. The low intensity of this excitation also means that we can neglect its harmonics as contributions to the scattering on either side of the fundamental at 744 cm^{-1} discussed above. The intensity on each side of the fundamental amounts to a third of the intensity in the central portion, a much greater amount than could be accounted for by harmonics of the 300-cm^{-1} vibration. Once again, we cannot tell whether this feature is introduced at the preparation stage or is the result of partial decomposition.

Acknowledgments

We are grateful to M. Fones of the Solid State Instruments Group, Harwell, for taking the X-ray diffraction patterns, and to Dr. M. W. Johnson of the Rutherford Laboratory for performing the multiple scattering corrections.

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