JOURNAL OF MATERIALS SCIENCE 33 (1998) 1949–1954

# Internal friction of amine-intercalated $TaS_2$

E. D. BRANDNER[*], A. MUNIER[*], J.-M. ZHU[‡], B. A. AVERILL[‡§], B.S. SHIVARAM[*]
*[‡]Department of Physics, and [‡]Department of Chemistry, University of Virginia*
*Charlottesville, VA 22901 USA*

Internal friction measurements on $TaS_2$ and a representative number of its amine intercalates are reported. The intercalants are observed to magnify the features seen in the internal friction curve of pure $TaS_2$ and to introduce new features such as abrupt decreases in internal friction (IF) attributed to the melting of certain intercalants and a large low-temperature IF peak attributed to thermally activated proton exchange among intercalant molecules. The intercalant configurations, host-layer separations, and the number of amine groups per intercalant molecule, are used to explain the differences seen in the internal friction spectra of the intercalated samples. © *1998 Chapman & Hall*

## 1. Introduction

Layered materials have a variety of unique properties, including the acceptance of guest molecules between their layers – a phenomenon called intercalation. Intercalation changes many of the other properties of the host material, as has been illustrated by a variety of experiments on layered transition metal dichalcogenides (i.e. $TaS_2$) which have observed changes in the hosts' lattice constants, superconductivity, ion and molecular transport, electrical and optical properties, etc. [1–7]. To our knowledge, very few internal friction studies on intercalated materials have been performed [8]; however, internal friction and acoustic attenuation measurements are powerful tools in analysing phase transitions and dislocation phenomena, as is observed in other systems [9].

In a previous study, we have shown that the internal friction of various layered compounds including graphite, several of the metal dichalcogenides, and certain montmorillonite clays show remarkable similarities [10, 11]. They all have a high-temperature (starting above 235 K) plateau, and at low temperatures (between 77 and 200 K), most have a weak internal friction peak that depends on the preparation and history of the sample [10, 11]. In graphite, tensile tests within a transmission electron microscope have shown that the high-temperature plateau corresponds to the motion of basal plane dislocations which can move in response to stresses only at high temperatures [12, 13]. Basal plane dislocation motion has also been observed in hydrazine-intercalated $TaS_2$ at and above room temperature – the onset of dislocation motion was apparently not explored [4]. Based on these studies and the similarity of the materials and their internal friction spectra, it was suggested that dislocation motion can also be used to explain the plateau seen in the other layered materials, including intercalated $TaS_2$ [8, 10, 11].

In the present paper, we report internal friction measurements on a representative number of amine-intercalated $TaS_2$ samples. These intercalates were chosen because the samples are relatively easily prepared, and the molecular orientation of the amine intercalants is well established [2, 14]. Further, they demonstrate the evolution of the internal friction as the intercalants change from a monolayer to a bilayer structure due to the lengthening of the amine chains. The monolayer intercalates measured were methylamine, pyridine, and ethylenediamine in $TaS_2$ (Fig. 1), and the bilayer intercalates measured were octylamine and octadecylamine in $TaS_2$ (Fig. 2) [2].

## 2. Experimental procedure

The specimens were compacted from intercalated powders. The host material was $TaS_2$ powder (99.8% pure) of 325 mesh size (44 μm) purchased from Johnson Matthey. It was intercalated by reacting it with the intercalants directly at 60–80 °C (150 °C for octadecylamine). The intercalation reaction was carried out for a number of days depending on the intercalant, and after complete intercalation, the powders were filtered and dried under vacuum. The samples were then pressed into bars by placing the intercalated powders into a hydraulic press for more than 20 h at 500 MPa. Finally, the compressed samples were cut into $40 \times 2.5 \times 0.7\ \text{mm}^3$ bars.

The internal friction of the specimens was measured by the "free–free bar" technique [9]. Each specimen was supported and pinned by four wires at its nodal

---

[*] *Present address*: Fonderie Affinage Et Recyclage De Metalux Precieux, CH-2800 Delemont, Switzerland.
[§] *Present address*: University of Amsterdam, Department of Biochemistry, Plantage Muidergracht 12, 1018 TV Amsterdam, The Netherlands.

0022–2461

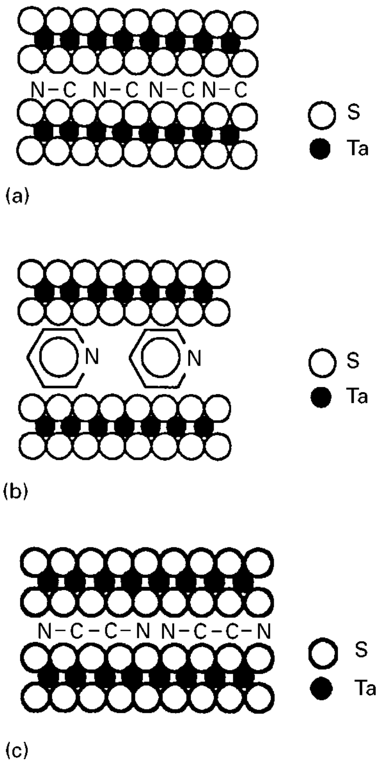

*Figure 1* The structure of $TaS_2$ intercalated with (a) methylamine ($CH_3NH_2$), (b) pyridine ($C_5H_5N$), and (c) ethylenediamine ($NH_2C_2H_4NH_2$) [2]. Hydrogen atoms are not shown.

points which were determined by the specimen's length. It was then excited at its resonant frequency using electrodes which were capacitively coupled to it and induced a strain of $< 10^{-5}$. After reaching its maximum amplitude, the excitation was abruptly terminated, and the free decay of the amplitude was recorded. An exponential fit to the free decay yields the internal friction (IF) [10, 11]. For each specimen, the internal friction was measured first from 80–355 K and again from 80–385 K in order to confirm the data and explore the effects of annealing on the specimens (except for the methylamine intercalated sample, no significant annealing effects were measured for the intercalated samples [8]). The data were recorded at 1 K temperature intervals at a heating rate of approximately 20 K $h^{-1}$.

## 3. Results

Fig. 3 compares the IF data for $TaS_2$ and its monolayer intercalates. The $TaS_2$ data exhibit a step at 270 K which levels out at an IF of 10. Following intercalation, the stepwise increase appears to be preserved but shifted to lower temperatures and to higher IF levels. In pyridine-intercalated $TaS_2$, a shoulder in the internal friction curve at a level of 12 is observed at 260 K. Following the shoulder, the internal friction rises to 29 at 340 K. The methylamine-intercalated sample's internal friction curve is very similar to that of the pyridine-intercalated sample. A shoulder occurs at a temperature of 245 K and a level of 11 followed by a final internal friction increase to 29 at 330 K. In addition, a small low-temperature peak is evident at 170 K in the methylamine sample. Ethylenediamine also has a low-temperature peak near 170 K, but unlike pyridine, methylamine, and pure $TaS_2$, no other feature exists until a peak of 50 is reached at 360 K.

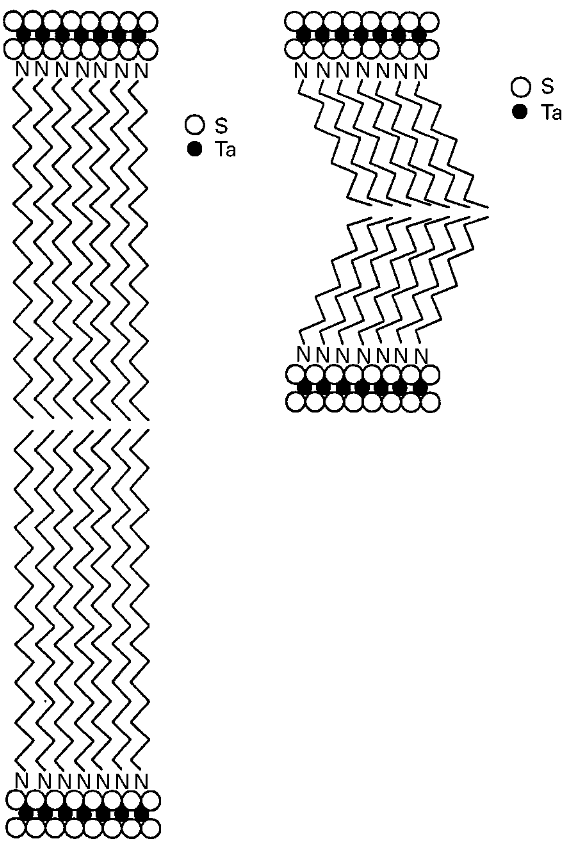

*Figure 2* The structure of $TaS_2$ intercalated with octylamine ($C_8H_{17}NH_2$) and octadecylamine ($C_{18}H_{37}NH_2$) [2]. Hydrogen atoms are not shown.

In Figs 4 and 5, the IF measurements of the bilayer intercalates (octylamine and octadecylamine) are presented along with that of $TaS_2$ as a reference. The bilayer intercalants drastically modify the internal friction spectrum of pure $TaS_2$. Each of them has an enormous low-temperature peak ($\sim 35$ at 120 K for octylamine and $\sim 50$ at 150 K for octadecylamine). Each peak is followed by a shoulder similar to the step seen in pure $TaS_2$ that occurs at $\sim 35$ and a temperature of $\sim 255$ K for octylamine and at 28 and a temperature of 260 K for octadecylamine. The internal friction levels further increase to approximately 50 in each of these samples and then plummet to 12 at 370 K for octylamine and at 330 K for octadecylamine. Octadecylamine has a final internal friction increase to 18 near the maximum temperature of these measurements (385 K). Fig. 5 also demonstrates the reproducibility of the measurements and the effects of annealing on two different octylamine samples.

## 4. Discussion

### 4.1. Internal friction steps below 360 K

### *4.1.1. 300–360 K*

Inspite of the wide range of behaviour observed in amine-intercalated $TaS_2$, we notice that all of the samples have an internal friction increase between 310 and 360 K (Figs 3, 4, and 5). Because this increase is

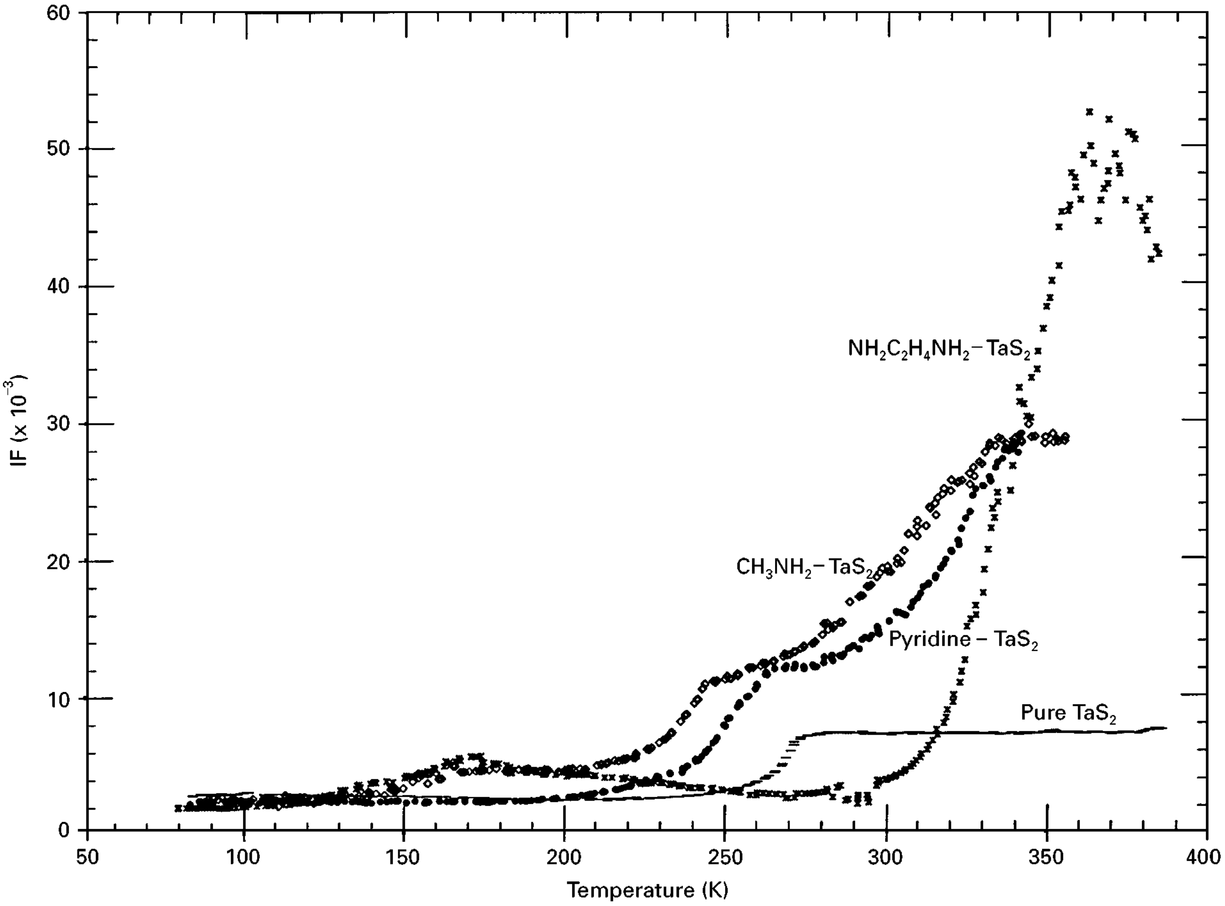

*Figure 3* The internal friction of $TaS_2$ and its monolayer intercalates: ethylenediamine–$TaS_2$, methylamine–$TaS_2$, pyridine–$TaS_2$.

common to all of the intercalates and the intercalant–host interaction is mediated by an amine group in all of them, we propose to associate this feature with the thermal breaking of the intercalant–host attraction. This thermal depinning allows basal plane dislocations to move independently of the intercalant molecules. Intercalant mobility [14] also contributes to the high IF at these temperatures in the monolayer intercalates. Also, such depinning is thought to be a prerequisite for the melting of the bilayer intercalants which occurs immediately after this peak for both octylamine and octadecylamine (Fig. 4) [15].

At these high temperatures, methylamine is the only sample which shows signs of deintercalation in repeated internal friction measurements as inferred by comparing X-ray diffraction spectra before and after the IF measurements [8].

Deintercalation does not occur until 470 K for octadecylamine-intercalated $TaS_2$ and not until 375 K for pyridine-intercalated $TaS_2$, as observed by thermogravimetric measurements [2, 15].

### 4.1.2. 200–300 K

Above 285 K, a plateau due to dislocation motion is observed for pure $TaS_2$ (Fig. 3) [10, 11]. The shoulder of a similar plateau is also observed for each of the intercalates which have only one amine group, although it is shifted to lower temperatures (240–270 K) and substantially higher magnitudes (Figs 3, 4, and 5). As with pure $TaS_2$, these steps are attributed to the motion of basal plane dislocations in response to the applied stresses at sufficiently high temperatures. As expected, the shoulders are magnified and shifted to lower temperatures by the intercalants because of the higher concentration of dislocations [16] and the broadening of the gap between host layers caused by intercalation. Because the thermal depinning of the host and the intercalates has not occurred at these temperatures, the dislocations are still pinned to the intercalants and drag them as they move. Therefore, for each intercalated sample, the temperature and height of the plateau will depend on the size of the intercalant, the intercalant–intercalant interaction, and the intercalant–host interaction.

The monolayer intercalates that exhibit this step (methylamine and pyridine) do not crystallize within the host [2]; therefore, the temperature and height of their steps is primarily determined by the size and mass of the dragged intercalant molecules and not by the intercalant–intercalant interaction. Of these two samples, methylamine, the lighter molecule, has the lower starting temperature and ending level of the step (Fig. 3).

Only ethylenediamine does not have a shoulder at or below 270 K that can be identified with the motion of basal plane dislocations in the $TaS_2$ lattice (Figs 3, 4, and 5) [10, 11]. Because the attraction between the intercalant and host is mediated by the amine groups, the dislocations in the diamine-intercalated sample must overcome both pinning sites of the diamine in order to move through the $TaS_2$ layer, dragging the

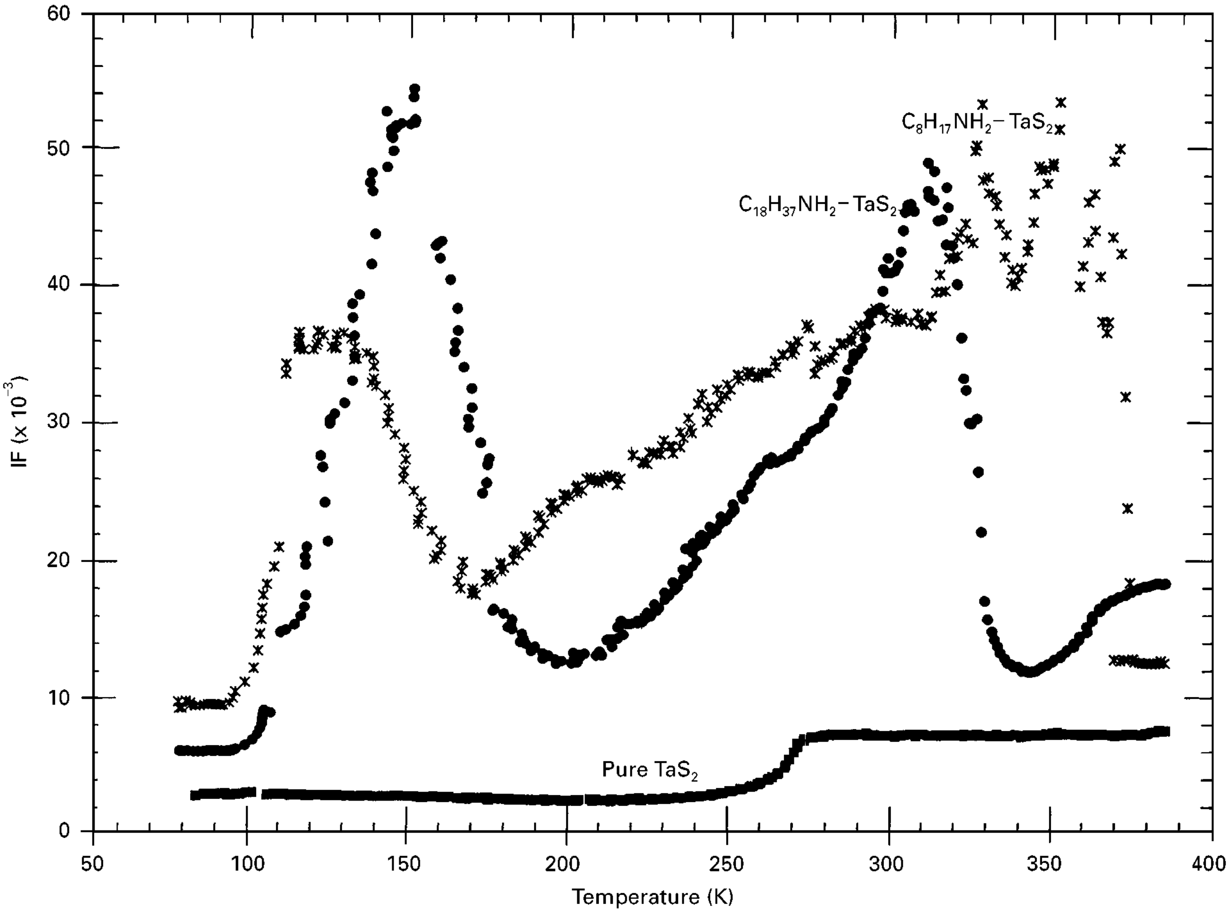

*Figure 4* The internal friction of $TaS_2$ and its bilayer intercalates: octylamine–$TaS_2$ and octadecylamine–$TaS_2$.

intercalant. No such effect is measured; therefore, the two pinning sites of the diamine apparently serve to anchor dislocations.

## 4.2. Low-temperature (below 200 K) internal friction peaks

The diamine, methylamine, and bilayer intercalates each have an internal friction peak at low temperatures (between 120 and 170 K). For the bilayer intercalates, this peak is one of the most outstanding features of their IF curves (Figs 3, 4, and 5). This represents the first observation of such a strong feature in the internal friction curves of layered materials at these temperatures. Therefore, in a search for a possible physical explanation of the origin of this peak, other related phenomena in intercalated layered compounds have been examined.

It has been suggested that the intercalation of the long-chain amines (greater than six carbons in $MoS_2$) into the metal dichalcogenides, proceeds because of the process of "protonation" [14, 17]. During this process, a certain fraction of the intercalant amine groups is provided with an extra proton that can be shared with neighbouring unprotonated intercalant molecules. Other evidence for proton exchange comes from angular correlation studies of the $\gamma$–$\gamma$ cascade of $^{181}Ta$ in samples of hafnium-doped $TaS_2$ intercalated with pyridine and ammonia [7]. By these experiments, the activation temperature for proton exchange in pyridine-intercalated $TaS_2$ occurs at ~60 K (below the minimum temperature of our measurements), and in ammonia-intercalated $TaS_2$, a broad transition starts below 50 K and ends near 100 K [7].

Proton exchange (or hoping of protons from site to site) is a process very similar to the motion of point defects in solids. Point defects are also known to cause enormous IF peaks and this phenomenon is well studied in several systems including iron and tantalum crystals containing interstitial hydrogen [9]. With these facts, we suggest that the observed low-temperature IF peaks are due to proton exchange between neighbouring intercalant sites. The low temperature of pyridine's activation temperature for proton exchange is believed to be due to the fact that its amine groups are not adjacent to the host layers, unlike the other measured intercalates. The greater host-intercalant interaction of the other intercalates is believed to hinder proton exchange requiring more thermal energy for the exchange to proceed and resulting in an IF peak in the temperature range of these measurements. Also, in the bilayer intercalates, the host–intercalant interaction may produce strain in the "frozen" [15] intercalant layers which is reduced by proton exchange and causes their large IF peak. However, in the monolayer intercalates, the peak can just as easily be explained by impurities as has been done for some pure layered materials which have similar peaks [11].

Because proton exchange appears to be highly dependent on the electrical properties of the $TaS_2$ host,

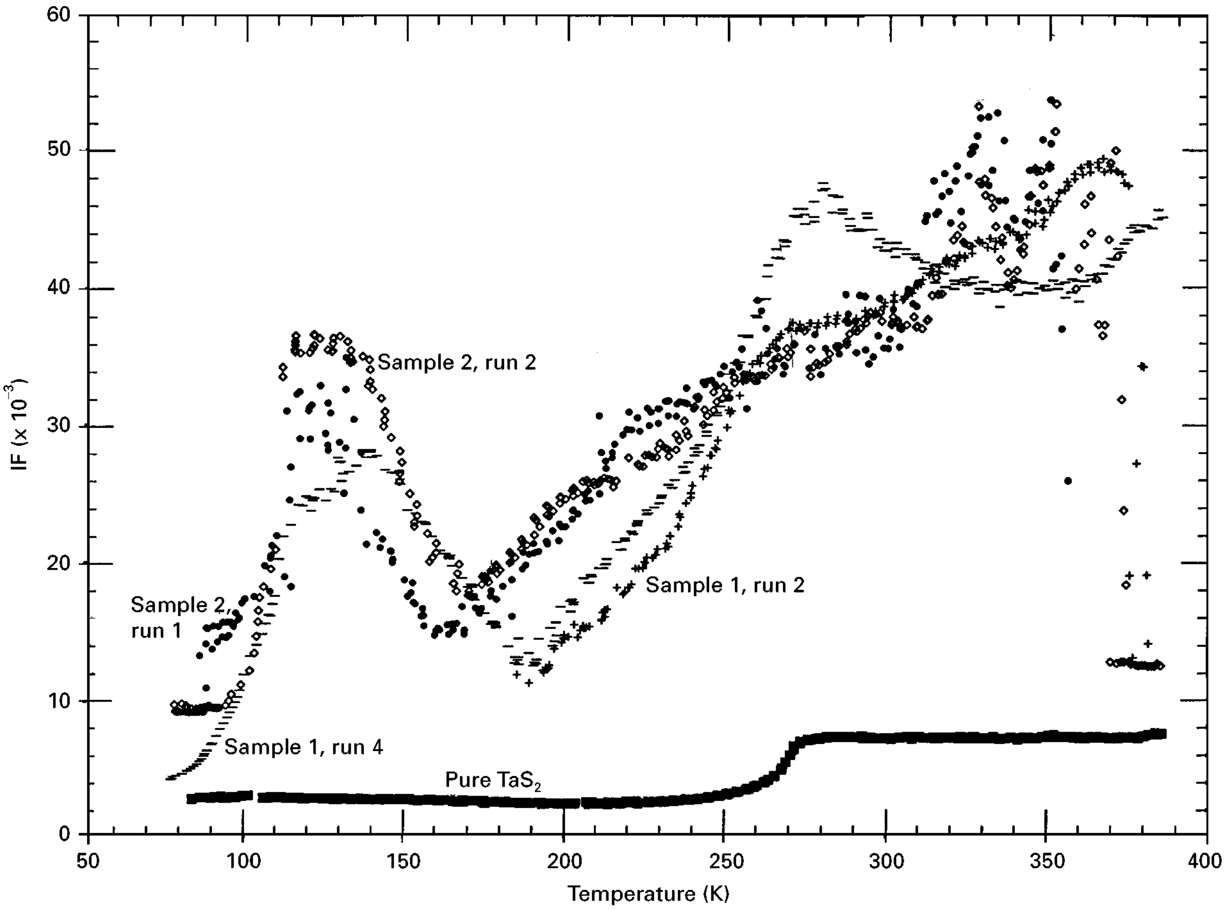

*Figure 5* The internal friction of $TaS_2$ and two different octylamine–$TaS_2$ intercalates.

resistivity measurements and electron density calculations on amine intercalates may prove useful in understanding this process. Resistivity curves of hydrazine-intercalated $TaS_2$ have a slight slope change near the temperatures of the low-temperature IF peaks, as observed by Sarma *et al*, but they do not address this feature [18]. $MoS_2$ intercalated with the long-chain amines apparently averages one protonated intercalant molecule for every seven – this is calculated knowing that for an intercalant chain length of six carbons or more the intercalant chains assume an orientation of 68° to the host layers instead of lying parallel to them [19]. Such a reorientation for amine-intercalated $TaS_2$ occurs for a chain length of four carbons [2] which corresponds to an area of 0.38 $nm^2$ per electron and, interestingly, an average distance between protonated intercalants similar to the wavelengths of the charge-density waves in $TaS_2$ [20]. This suggests a possible link between the charge-density waves and the low-temperature IF peaks.

## 4.3. Unique features of the bilayer intercalates above 300 K

### 4.3.1. Melting

Following the thermal depinning of the host from the guest, the bilayer intercalates have a sharp drop in their internal friction spectra caused by the melting of the intercalants (Fig. 4) [15] This decrease begins at 325 K (ending at 345 K) for octadecylamine whose bulk melting point is 326 K and at 370 K for octylamine whose bulk melting point is 273 K (Fig. 4) [21]. Differential scanning calorimetry (DSC) measurements performed by Dines on octadecylamine intercalated $TaS_2$ show that the intercalant melt occurs at 348 K (beginning at 320 K) [15]. Nuclear magnetic resonance measurements confirm that the octadecylamine intercalate shows crystalline-like behaviour at room temperature and liquid-like behaviour at 350 K [15].

Because the bilayer intercalates' melting temperatures are both above their bulk melting temperatures (Fig. 4) [15], the intercalant–host interaction must play a significant role in the melting transition. The crystalline structures of the intercalant bilayers indicate just how strong this interaction is. The octylamine's intercalant–host attraction forces each molecule to tilt 56° from the host plane (Fig. 2), but for the octadecylamine intercalate, the intercalant–intercalant bonds are strong enough to force a molecular orientation perpendicular to the host plane (Fig. 2) [2]. Smaller angles between the intercalant molecules and the host layers are expected to be more favourable to the host because less energy is expended in spreading the host-layers apart. This indicates that the host has a greater effect on the molecular orientation of the octylamine and its melting temperature than on the molecular orientation of the octadecylamine (Fig. 2). Therefore, the melting of the octylamine intercalant occurs at a higher temperature than the melting of the octadecylamine intercalant (Fig. 4).

### 4.3.2. Internal friction step near 360 K

The DSC measurements of Dines [15] also indicate an intercalant phase change at 363 K for octadecylamine which corresponds to the beginning of the last internal friction increase observed in the octadecylamine intercalate (Fig. 4). This feature may be explained by an intercalant configuration change similar to that seen in $NbS_2$ intercalated with octadecylamine where the intercalant molecules relax, and a $c$-axis contraction from 5.86 nm to 4.61 nm takes place [2, 22]. Such a reduction in the layer separation is more favourable to the host but would be possible only after the intercalant melts.

## 5. Conclusion

Internal friction measurements on amine-intercalated $TaS_2$ have shown that the intercalants magnify the energy dissipation of the host under applied stresses above a characteristic temperature. The inertia of the intercalants, the increased density of dislocations caused by intercalation [16], and the spreading of the host layers [2] all contribute to this effect. Further, all of the amine intercalants have a huge internal friction increase near 350 K which is attributed to the disassociation of the host from the amine group which mediates the host–intercalant interaction.

Dramatic IF effects were observed in the bilayer intercalates due to the interaction between the host and intercalant lattices. Intercalant melting was observed in the octylamine and octadecylamine intercalates [15]. A huge low-temperature IF peak was also observed in these intercalates which is likely caused by the onset of proton exchange among intercalants.

Beyond the effects of amine intercalants on the IF curves of $TaS_2$, these experiments demonstrate that IF measurements are sensitive to restricted geometry phenomena such as melting and other phase changes. In addition, this work suggests possible ways of engineering new high-damping materials by intercalation chemistry.

## Acknowledgement

This work was supported by the Office of Naval Research Materials Division (N00014-91-J-1962).

## References

1. R. BREC and J. ROUXEL, in "Intercalation in Layered Materials", edited by M. S. Dresselhaus (Plenum Press, New York, 1986) p. 75.
2. A. L. JACOBSON, in "Intercalation Chemistry", edited by A. L. Jacobson and M. S. Whittingham (Academic Press, New York, 1982) p. 229.
3. M. SARMA, A. R. BEAL, S. NELSON and R. H. FRIEND, *J. Phys. C* **15** (1982) 477.
4. G. J. TATLOCK and J. V. ACRIVOS, *Philos. Mag. B* **38** (1978) 81.
5. A. H. THOMPSON and F. J. DISALVO, in "Intercalation Chemistry", edited by A. L. Jacobson and M. S. Whittingham (Academic Press, New York, 1982) p. 573.
6. A. H. THOMPSON, F. R. GAMBLE and R. F. KOEHLER, *Phys. Rev. B* **5** (1972) 2811.
7. T. BULZ, A. VASQUEZ, H. SAITOVITCH and R. MUHLBERGER, *Physica* **99B** (1980) 69.
8. B. A. AVERILL, J.-M. ZHU, T. E. SUTTO, A. MUNIER and B. S. SHIVARAM, in "Damping of Multiphase Inorganic Materials", edited by R. B. Bhagat (ASM International, Materials Park, OH, 1993) p. 171.
9. A. S. NOWICK and B. S. BERRY, "Anelastic Relaxation in Solids" (Academic Press, New York, 1972).
10. E. D. BRANDNER, A. MUNIER, J.-M. ZHU, B. A. AVERILL and B. S. SHIVARAM, *J. Appl. Phys.* **76** (1994) 7784.
11. A. MUNIER, J.-M. ZHU, T. E. SUTTO, B. A. AVERILL and B. S. SHIVARAM, in "Damping of Multiphase Inorganic Materials", edited by R. B. Bhagat (ASM International, Materials Park, OH, 1993) p. 9.
12. P. MILLET, R. SCHALLER and W. BENOIT, *J. Phys. Colloq.* **46** (1985) C10-405.
13. R. SCHALLER and W. BENOIT, in "Proceedings of the 56th World Foundary Congress", Dusseldorf, Germany, May 1989, p. 13.2.
14. R. SCHÖLLHORN, in "Intercalation Chemistry", edited by A. L. Jacobson and M. S. Whittingham (Academic Press, New York, 1982) p. 315.
15. M. B. DINES, *Inorg. Chem.* **17** (1978) 763.
16. M. J. McKELVEY, R. SHARMA and W. S. GLAUSINGER, *Solid State Ionics* **63–65** (1993) 369.
17. R. SCHÖLLHORN, H. D. ZAGEFKA, T. BUTZ and A. LERF, *Mater. Res. Bull.* **14** (1979) 369.
18. M. SARMA, A. R. BEAL, S. NULSEN and R. H. FRIEND, *J. Phys. C* **15** (1982) 477.
19. R. SCHÖLLHORN and A. WEISS, *J. Less-Common Metals* **36** (1974) 229.
20. W. Y. LIANG, in "Intercalation in Layered Materials", edited by M.S. Dresselhaus (Plenum Press, New York, 1986) p. 31.
21. "CRC Handbook of Chemistry and Physics", 66th edn (CRC Press, Boca Raton, FL, 1985) pp. C-380, C-381.
22. R. SCHÖLLHORN, E. SICK and A. WEISS, *Z. Naturforsch* **28B** (1973) 168.

*Received 20 February*
*and accepted 1 December 1995*