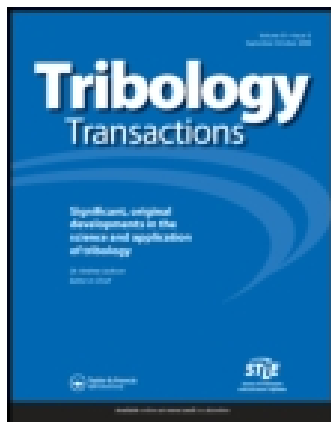


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Crystal Chemistry and Solid Lubricating Properties of the Monochalcogenides Gallium Selenide and Tin Selenide

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Crystal Chemistry and Solid Lubricating Properties of the Monochalcogenides Gallium Selenide and Tin Selenide[©]

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The interatomic array and bond structure in crystalline states of the monochalcogenides tin selenide and gallium selenide are described and correlated with their solid lubricating capacity. Friction tests assessing their solid lubricating performance were carried out on a pin-on-disk machine. Specifically, large crystalline pieces of each inorganic solid were cut and cleaved into flat squares and subsequently rubbed against sapphire balls. In another case, fine powders of gallium selenide and tin selenide were manually fed into the sliding interfaces of 440C pins and 440C disks. For the specific test conditions explored, friction coefficients of the sapphire/gallium selenide and sapphire/tin selenide pairs were approximately 0.23 and approximately 0.35, respectively. The friction coefficients of 440C pin/440C disk test pairs with gallium selenide and tin selenide powders were approximately 0.22 and approximately 0.38, respectively. For comparison, a number of parallel friction tests were also performed with MoS₂ powders and compacts, and the results of these tests are reported. The friction data, together with the crystal-chemical knowledge and electron microscopy evidence, supported the conclusion that the solid lubricating capabilities and lubrication mechanisms of these solids are closely related to their crystal chemistry and the nature of their interlayer bonding.

KEY WORDS

Solid Lubrication, Friction

INTRODUCTION

This paper describes the interatomic array and bond structure of the monochalcogenides tin selenide (SnSe) and gallium selenide (GaSe), and correlates this knowledge with their solid lubricating performance and mechanisms. Like the transition-metal dichalcogenides (e.g., MoS₂, WS₂, and WSe₂ which are well-known solid lubricants), SnSe and GaSe

crystallize as layered structures and have fairly high melting points of 861°C and 960°C, respectively. SnSe and GaSe are known as sandwich semiconductors in solid-state physics (1), (2), and have been studied rather extensively by physicists in the past. However, their tribological properties and potential uses in friction and wear applications have not yet been explored in much detail. As will be elaborated later, SnSe represents a group of layered compounds that also comprise SnS and the sulfides and selenides of germanium, whereas GaSe belongs to a class that also includes the layered GaS and the sulfides and selenides of indium.

Previous research on solid lubrication has largely concentrated on transition-metal dichalcogenides and demonstrated that among numerous kinds, only a few are capable of imparting low friction to sliding tribological interfaces. For example, it was found that despite their layered crystal structures, NbS₂, TiS₂, VS₂, TaS₂, etc., are not as lubricious as MoS₂ or WS₂ (3), (4). Based on the molecular orbital and valence bond theories, Jamison proposed the following explanation for the poor lubricating performance of NbS₂, TiS₂, VS₂, TaS₂, etc. (4), (5): in the layered crystal structure of these solids, there is a region of negative electrical charge that not only concentrates above the chalcogen atoms of a given layer but also extends well into the pockets between the chalcogen atoms of neighboring layers. Because the bottoms of the pockets are positively charged (due to exposed ion cores of the surrounding atoms), an electrostatic attraction exists between the layers, making the layers of these solids shear with difficulty.

As for the excellent solid lubricating capacities of MoS₂ and WS₂, the region of negative electrical charge is contained within the layers. Thus, the surface of the chalcogen atoms is positively charged, creating an electrostatic repulsion between the layers, and making interlayer slippage exceedingly easy (4). Relatively larger interlayer separation in MoS₂ and WS₂ crystals is thought to result from the same electrostatic repulsion between successive layers. In general, these and other studies have supported the conclusion that not all layered structures are good solid lubricants (4). The type and magnitude of interlayer bonds are also critically important.

Although GaSe and SnSe have attracted a great deal of attention in solid-state physics for microelectronics and optical applications (1), (2), their lubrication mechanism and potentials for tribological applications have remained relatively unexplored. In a series of studies by Boes (6), Boes and Chamberlain (7), Kiparisov et al. (8), and Gardos (9), the tribological and thermal oxidation properties of a composite lubricant consisting of indium/gallium and WSe₂ were reported. The principal goal of these studies was to achieve better oxidation resistance on WSe₂ by alloying it with low-melting point indium and gallium. Upon curing the composite mixture at high temperatures, the investigators found that both indium and gallium underwent chemical reaction with WSe₂ to form the selenides of these metals. They also demonstrated that compared to the parent WSe₂, the new composite lubricant exhibited superior oxidation resistance over a wide range of temperature. Also, the lubricating capability of this new lubricant was much superior to that of WSe₂ alone, especially at elevated temperatures (8).

More detailed studies by Kiparisov et al. (8) and Gardos (9) elaborated the mechanism of the improved oxidation resistance of the indium/gallium/WSe₂ lubricant. According to Gardos, a protective film resulting mainly from the preferential oxidation of substoichiometric InSe was primarily responsible for the superior oxidation resistance of this new lubricant. The protective film was thought to effectively shield the lubricating entities against oxidation.

The primary goals of this paper are to describe in detail the crystal chemistry of the monochalcogenides GaSe and SnSe, to ascertain their lubricating capabilities, and to combine crystal-chemical knowledge with lubrication performance to elucidate their solid lubricating mechanisms. The knowledge gained through this study can help enhance the general understanding of the lubricating mechanisms of inorganic solids with layered structures.

CRYSTAL CHEMISTRY AND BOND STRUCTURE

GaSe

GaSe has been reported to exist as a layered structure in four crystallographically distinct polytypes, i.e., β -, ϵ -, δ -, and γ -GaSe (10), (11). Each polytype results from the stacking of layers in different ways. Specifically, the different coordination symmetry of the metal atoms in a layer and the dissimilar stacking order of each layer in the unit cells are different in each polytype (10). The β -, δ - and ϵ -types have a layered hexagonal crystal structure (1), (10), (12), whereas the γ -type crystallizes in a rhombohedral structure (13). Because of their lamellar structures, all the crystalline polytypes mentioned above may have some solid lubrication capabilities. In particular, β -GaSe has a crystal structure and bond characteristics similar to that of MoS₂, a popular solid lubricant (10), (12), (14). Therefore, it has the potential to impart low friction to sliding interfaces and this paper will focus on the crystal chemistry and tribology of a β -GaSe. For brevity, the chemical symbol GaSe will refer to the β -GaSe in the following sections. Micro-laser Raman spectroscopy was used to verify that the GaSe material used in this study was β -GaSe.

As illustrated in Fig. 1, the structure of GaSe consists of layers that can be regarded as a two-dimensional sheet of closely packed and strongly bonded Ga and Se atoms in the sequence Se-Ga-Ga-Se (1), (10), (12), (15). Each layer consists of four atomic planes. The Ga atoms are paired to form the two atomic planes inside, while the Se atoms form the top and bottom planes. The interatomic bonding within the layers is strong and mainly of the covalent type, whereas the bonding between adjacent layers is weak and of the van der Waals type (1), (10), (12). Because of such strong anisotropy in bonding, solid crystallites of GaSe can easily be cleaved along the basal planes.

According to Zallen and Slade (12), the structures of GaS and/or GaSe are closely related to that of MoS₂. In fact, removal of one layer of Ga atoms in the GaSe crystal structure, shown in Fig. 1 produces the exact crystal structure of MoS₂ illustrated in Fig. 2. Table 1 presents the unit cell

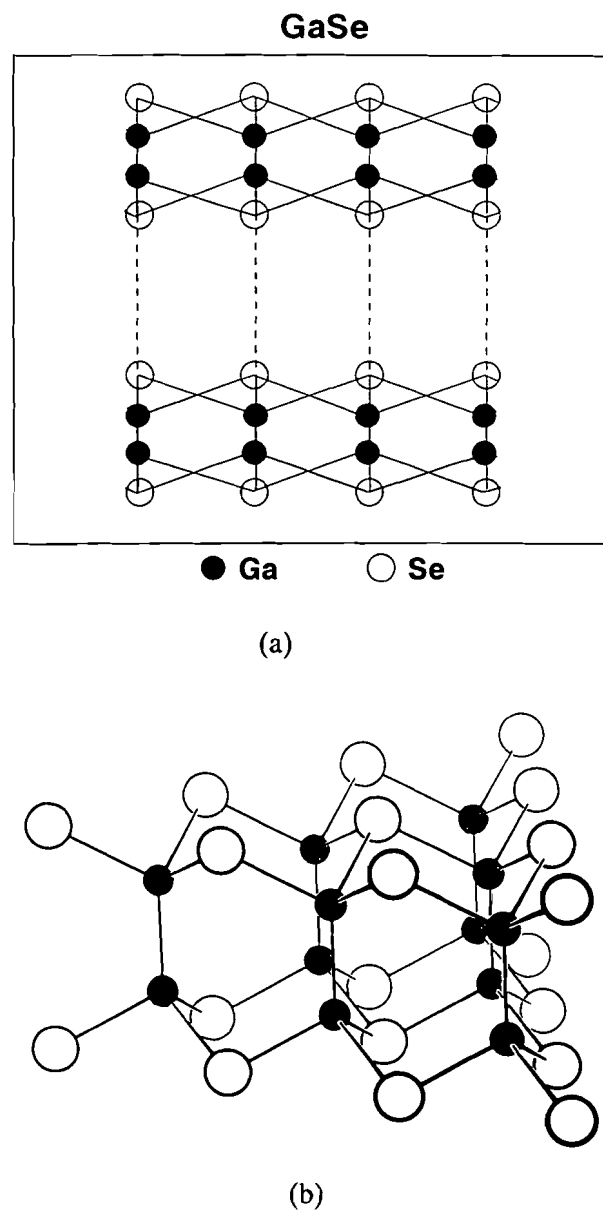


Fig. 1—(a) Schematic illustration of layered-hexagonal structure of GaSe. (b) Interatomic configuration and bonding in a layer of GaSe. Black circles represent Ga atoms.

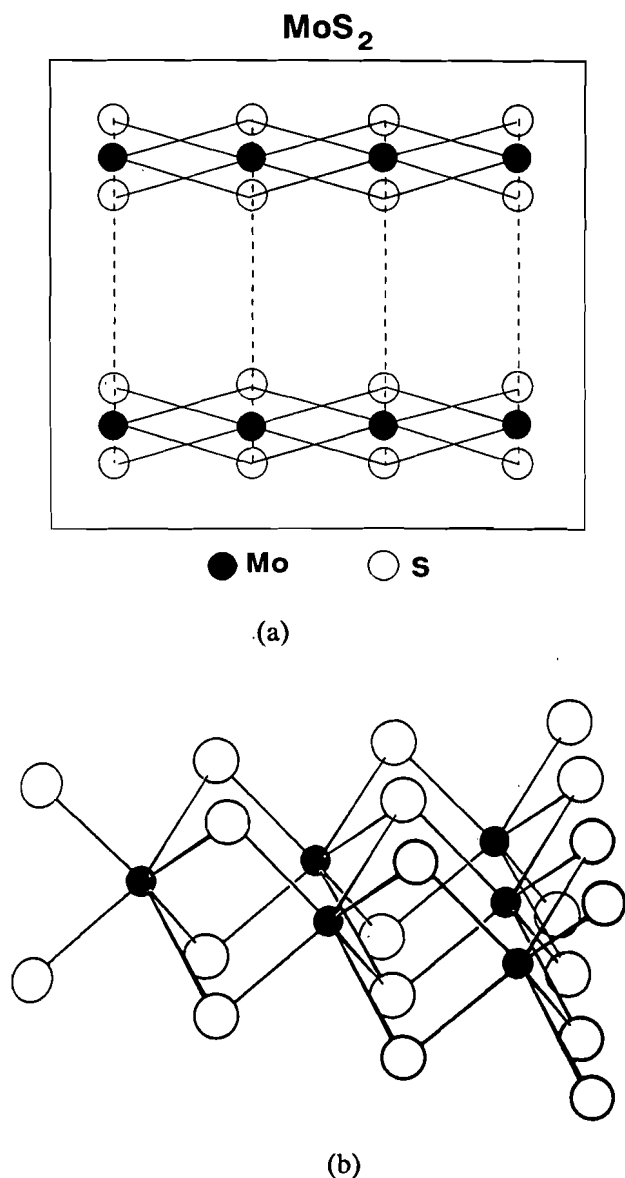


Fig. 2—(a) Schematic illustration of layered-hexagonal structure of MoS₂. (b) Interatomic configuration and bonding in a layer of MoS₂. Black circles represent Mo atoms.

parameters of GaSe for comparison, and the cell parameters of MoS₂ are also included. The interlayer-to-intralayer bond-length ratio for a given layered solid is reported to be a crude but revealing structural measure of the layerlike character of that solid (12). In general, the greater the interlayer-to-intralayer bond-length ratio, the weaker the interlayer

bonding with respect to the intralayer bonds. For MoS₂ and GaSe crystals, the interlayer-to-intralayer bond length ratios were estimated to be 1.5 and 1.6, respectively (12). This suggests that MoS₂ and GaSe are structurally similar and have comparable layerlike characteristics. Within the rigid two-dimensional layers of MoS₂ crystals, the S atoms have a trigonal prismatic coordination around the Mo atoms, shown in Fig. 2b (14). The Ga atoms in the GaSe structure are tetrahedrally coordinated as shown in Fig. 1(b) (10).

SnSe

SnSe has an orthorhombic crystal structure consisting of two-dimensional sheets of strongly bonded Sn and Se atoms (2), (16)–(18). As illustrated in Fig. 3, the unit cell of SnSe consists of eight atoms and is two layers thick. The Sn and Se atoms are joined with strong heteropolar bonds to form the crystalline layers made up of two planes of zigzag Sn-Se-type chains (2).

Each atom in a layer is connected to its near neighbors with six heteropolar bonds. The three strongest bonds, denoted in Fig. 3 with solid lines, are established with the three nearest neighbors lying in the same layer. Two weaker bonds, denoted in Fig. 3 with broken lines, are with the more distant neighbors, again in the same layer, while the last and weakest bond is formed with an atom in the adjacent layer. Hence bonding between layers is a combination of van der Waals and weak electrostatic attractions. The cell parameters of the SnSe crystal structure are given in Table 1 (2), (16), (17).

As is clear from the foregoing, the crystal structure and bond characteristics of GaSe are similar in nature to those of MoS₂. Also, the interlayer bonding in GaSe (and MoS₂) across the cleavage plane is between like atoms, i.e., Se---Se (and S---S). Mainly because of a similar crystal structure and interlayer bonding, it is plausible that GaSe can also have some lubricating capability, possibly comparable to that of MoS₂. For SnSe, however, the relatively stronger interlayer bonding may prevent this compound from being as lubricious as MoS₂ or GaSe. Also, the interlayer bonding in SnSe across the cleavage plane is between unlike atoms, i.e., Sn---Se as shown in Fig. 3.

EXPERIMENTAL DETAILS

To elucidate the lubricating capabilities of GaSe and SnSe, a series of rudimentary friction tests was performed with the flat pieces and powders of these solids on a conventional

	SnSe	GaSe	MoS ₂
<u>Cell Dimensions (nm)</u>			
a	0.446	0.374	0.316
b	0.419	—	—
c	1.157	1.588	1.229
Interlayer chalcogen-chalcogen spacing	0.34	0.38	0.347
Unit cell	Orthorhombic	Hexagonal	Hexagonal

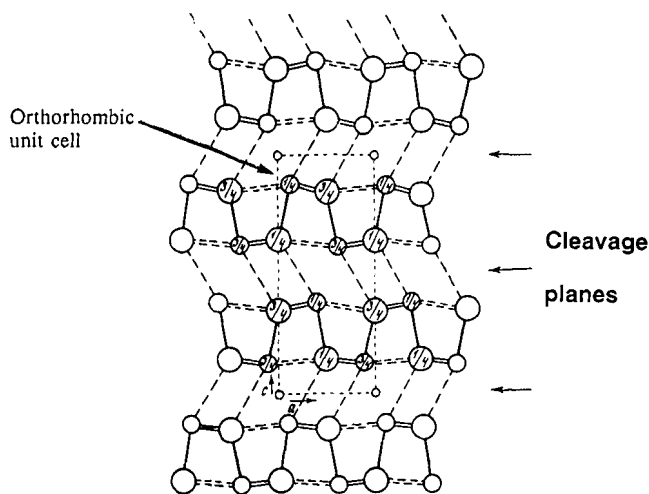


Fig. 3—Schematic illustration of layered-orthorhombic structure of SnSe. Large circles represent Se atoms, small circles represent Sn atoms.

pin-on-disk machine. The primary purpose of these friction tests was to explore the solid lubricating capabilities of GaSe and SnSe and to establish model relationships between their crystal chemistry and frictional performance. More detailed tests aimed at elucidating the possible roles of several test parameters (e.g., load, speed, distance, humidity, temperature) in the lubrication performance of these solids were not performed in this initial study. However, the scope of work was expanded to include MoS₂ as a reference material and to provide a basis for comparison with the friction test results from GaSe and SnSe.

As mentioned earlier, GaSe exists as a layered structure in four crystallographically distinct polytypes, β -, ϵ -, δ , and γ -GaSe (10), (11). The specific GaSe material used in this study was characterized by micro-laser Raman scattering experiments performed with an Ar ion laser. The Raman spectrometer was equipped with a photomultiplier tube as the detector and photon counting electronics. The laser light (487.9 nm at 50 mW) was focused on the sample through an optical microscope to a spot size of approximately 1.5 μm with a 100X objective in a strict 180° backscattering geometry.

Two types of friction tests were performed with the solid GaSe and SnSe materials. In one case, fairly large crystalline pieces of GaSe and SnSe were first cleaved into flat pieces, and then cut into squares with typical dimensions of approximately 1.5 cm \times 1.5 cm, and 1 to 2 mm thick. According to the technical specifications of the commercial source (19), the solid lumps of SnSe and GaSe were 99.98 wt.% pure. The squares were then firmly attached to a 5-cm-diameter steel disk and rubbed against sapphire balls in a pin-on-disk machine under the sliding conditions given in Table 2 and in the figure captions. In another case, fine powders of GaSe and SnSe with a particle size of approximately 50–100 μm were manually fed into the sliding interfaces of 440C pins and 440C disks. The pin-on-disk machine used in this study was calibrated by applying incremental forces to the pin holder in the tangential direction with the increments ranging from 0.2 to 0.5 N, depending on normal force, i.e., 2 N or 5 N. The MoS₂ test material included disk-shaped-compacts with a nominal diameter of approx-

PARAMETERS	SELECTED VALUE
Load (N)	2 and 5
Sliding velocity ($\text{mm}\cdot\text{s}^{-1}$)	1.7 to 5
Relative humidity (%)	8 to 27
Number of revolutions	500 to 1200
Ambient temperature ($^{\circ}\text{C}$)	23 ± 1
Number of tests	2 to 3

imately 2.5 cm and fine powders of approximately 10–20 μm size. The compacts were fabricated from the powders by cold pressing at approximately 35 MPa. It is conceivable that this type of unidirectional cold-pressing may result in some degree of preferred orientation in the final compacts, and this may affect the frictional behavior of sliding test pairs.

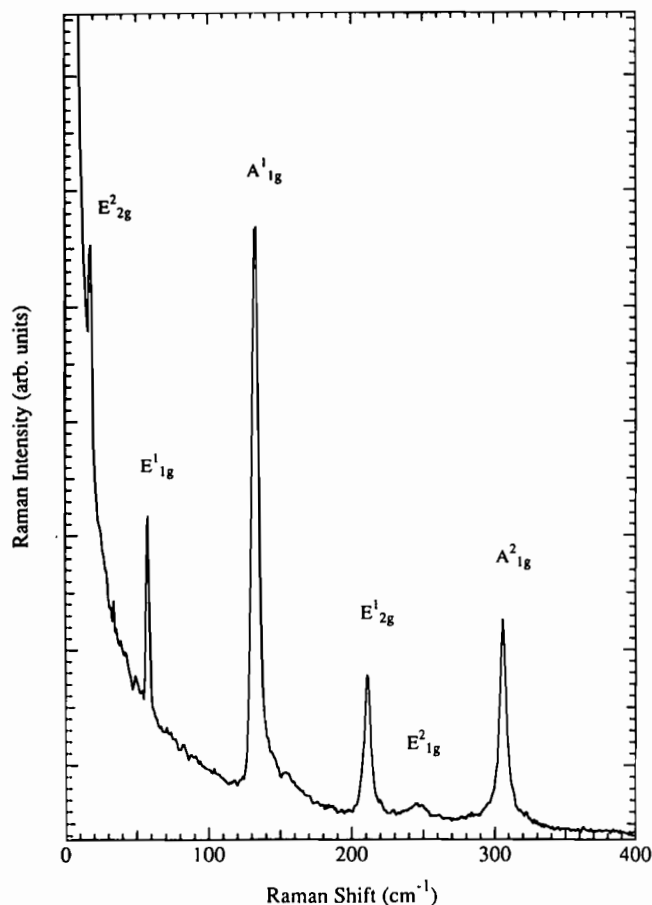
The Vickers hardness values of the 440C pin and disk specimens used in the friction tests were about 7.8 GPa. The surface finish of 440C disks was approximately 0.1 μm center-line-average (CLA), while that of the pin was approximately 0.02 μm CLA. One end of each pin was rounded to a radius of curvature of 127 mm. The sapphire balls were 6.35 mm in diameter and had a Vickers hardness value of approximately 22.5 GPa. The surface finish of these balls was better than 0.01 μm CLA. Two to three tests were run under each condition to verify the reproducibility of the friction data. The results were quite reproducible. The deviations from the mean friction values were in the range of $\pm 5\%$ and $\pm 10\%$, depending on test pairs and contact load.

RESULTS AND DISCUSSION

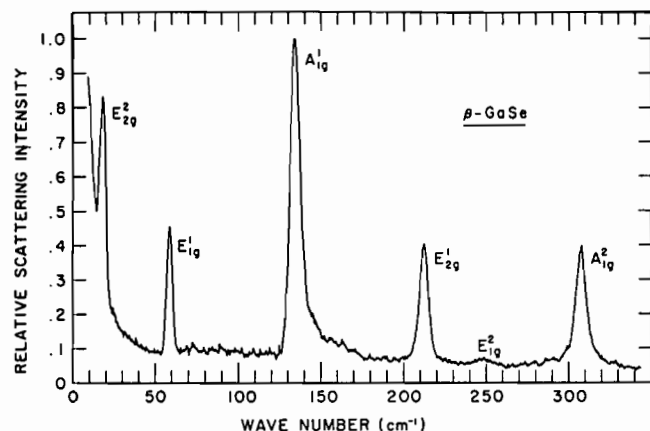
The Raman spectrum of the GaSe material used in this study reveals five strong Raman lines centered at 17.99, 57.99, 132.99, 210.99, and 305.99 cm^{-1} , as shown in Fig. 4(a). As is clear, this spectrum is very similar to the Raman spectrum of β -GaSe, as shown in Fig. 4(b), reported by Wieting and Verble (20). This confirms that the GaSe material used in this study was β -type.

Figure 5(a) shows, as a function of sliding cycles, friction coefficients of the 440c/440C test pairs including GaSe and MoS₂ powders at sliding interfaces. Initially, the friction coefficients of these test pairs were comparable, e.g., approximately 0.22 to 0.23. During successive sliding cycles, they increased slightly. The friction coefficient of a test pair including GaSe powders eventually reached a steady-state value of 0.24 after about 150 revolutions, whereas the friction coefficient of a test pair including MoS₂ powders decreased slightly with increasing sliding cycles, and stabilized at approximately 0.22.

Figure 5(b) shows friction coefficients of test pairs of sapphire/GaSe flat and sapphire/MoS₂ compacts. Initially, the friction coefficients of sapphire/GaSe and sapphire/MoS₂ pairs were quite different. As is evident, the friction coefficient of the sapphire/MoS₂ pair was initially approximately 0.3, but decreased steadily with sliding cycles and reached a steady-state value of approximately 0.25 after about 200 revolutions. Conversely, the initial friction coefficient of the



(a)



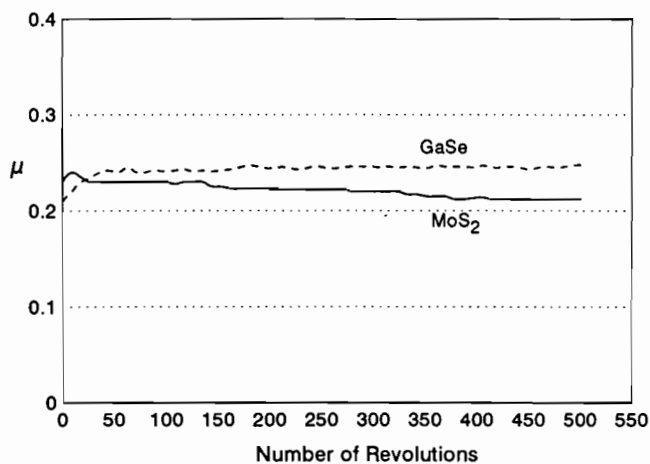
(b)

Fig. 4—Raman spectra.

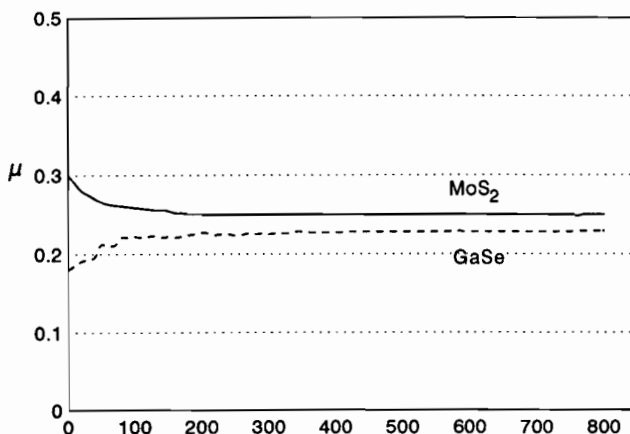
(a) GaSe material used in the study.

(b) β -GaSe reported by Wieting and Verbie (19)

sapphire/GaSe pair was approximately 0.18. However, it tended to increase slightly with sliding cycles and eventually reached a steady-state value of approximately 0.23 after about 100 revolutions. The results of this and previous experiments suggest that GaSe, like MoS₂, is a lubricious compound.



(a)



(b)

Fig. 5—Variation of friction coefficients as a function of sliding cycles.

(a) 440C pin/440C disk test pairs lubricated with GaSe and MoS₂ powders (relative humidity 14 percent)(b) sapphire ball/GaSe and MoS₂ flats (relative humidity 18 percent, load = 2N, temperature = 23°C, sliding velocity = 3.7 and 5 mm·s⁻¹, radius of curvature of 44C pin = 127 mm; radius of sapphire ball = 3.17 mm)

The initially high friction coefficient of the sapphire/MoS₂ pair in Fig. 5(b) can be attributed to the relatively random orientation of MoS₂ crystals in the as-compacted form. It can be argued that those randomly oriented crystallites will shear with greater difficulty, and thus cause a relatively high frictional force. However, under the influence of tangential forces of sliding contact, these crystallites eventually align themselves to assume an orientation parallel to the sliding direction that is much easier to shear, thereby attaining a relatively low steady-state friction coefficient, as shown in Fig. 5(b). Conversely, the relatively steady friction coefficient of the sapphire/GaSe system may have been achieved because the platelike crystallites of GaSe were already oriented parallel to the sliding direction.

Note that the friction coefficients of tribosystems with MoS₂ powders or compacts shown in Fig. 5 are somewhat higher than the 0.1 to 0.18 values reported by other researchers under sliding conditions of low (i.e., approximately one percent) to moderate (i.e., 40 to 60 percent) humidity and at higher contact pressures (3), (21)–(23).

This discrepancy may have been due to the difference in the purity and the moisture content of the MoS₂ used in this and other studies. The MoS₂ lubricant used in this study was 98.5 percent pure. Over time, it may have accumulated some moisture from the environment; hence, the higher friction coefficients here may have been due to excess moisture. Also, the different test conditions such as velocity, load, contact configuration, etc., used in this and previous studies may have contributed to the discrepancy.

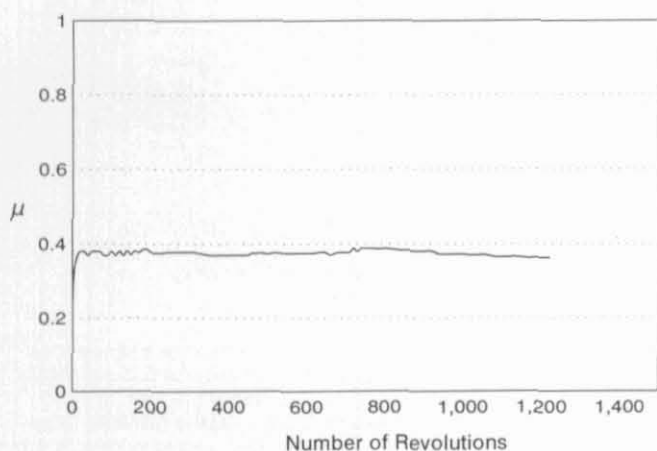
Figure 6 shows the sliding friction coefficient of a 440C pin/440C disk pair lubricated with SnSe powders and of the sapphire/SnSe test pair. The friction coefficient of SnSe powder-lubricated 440C pin/440C disk system shown in Fig. 6(a) was nearly constant at approximately 0.38 throughout the sliding test. However, the friction coefficient of a sapphire ball against SnSe was initially approximately 0.23, but eventually increased to approximately 0.35 after 60 revolutions, where it remained constant until the sliding test ended, as shown in Fig. 6(b). It is important to note that these friction values are significantly higher than those at-

tained with MoS₂ or GaSe. Such a discrepancy may have occurred because successive layers in the SnSe crystal are bound to each other with a combination of van der Waals and long-range electrostatic attractions, whereas, in the MoS₂ and GaSe crystals, the interlayer attraction was primarily of the van der Waals type. This observation further supports the notion that not all layered structures are good solid lubricants (4). The type and magnitude of interlayer bonds are also important. Based on these initial results, it can be deduced that compared to MoS₂ and GaSe, SnSe is a relatively poor lubricant.

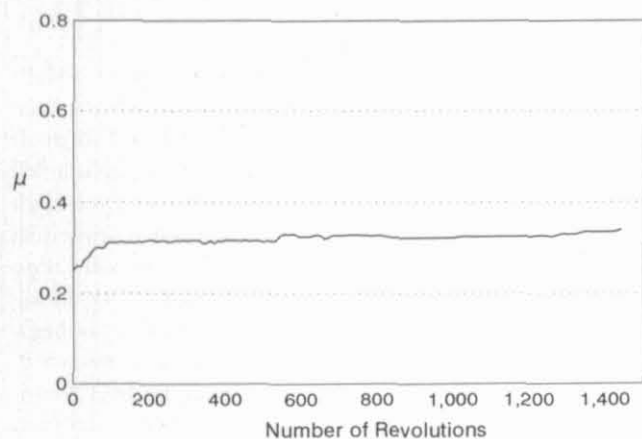
The wear of 440C pins and disks used in friction tests was hard to measure by surface profilometry or optical microscopy. Microscopic inspection of the wear scars and tracks indicated that GaSe, MoS₂, and SnSe were effectively smeared or burnished onto the sliding contact surfaces. As an example, Fig. 7 shows the general morphology of smeared GaSe on a 440C pin. After wiping off the excess lubricant and re-examining the surface with an optical microscope at 500X, some scratches became visible on both the scars and the tracks.

To elucidate the structural conditions of GaSe and SnSe before and after friction tests, scanning electron microscopy (SEM) was employed on free-standing as well as friction-tested particles of these solids. The SEM micrographs in Figs. 8 and 9 reveal that both the free-standing (untested) and friction-tested particles of these solids are made up of platelike crystallites. In both the free-standing and friction-tested forms, these crystallites are stacked on top of each other. This is consistent with the layered-crystal structure of these solids shown in Figs. 1 and 3. Noticeable in Figs. 8(b) and 9(b) is the manifestation of some intercrystallite slip between platelike crystallites, possibly due to the frictional traction that may have been incurred during sliding contacts.

Based on SEM evidence and the results of friction tests, it is hypothesized that, like MoS₂, the low-friction characteristics of GaSe and SnSe are primarily governed by their layered-crystal structures and interlayer bonding. It is con-



(a)



(b)

Fig. 6—Variation of friction coefficients as a function of sliding cycles.

(a) 440C pin/440C disk test pairs lubricated with SnSe powders (load = 1N, relative humidity = 27 percent)

(b) sapphire ball/SnSe flat (load = 5N, relative humidity = 8 percent, temperature = 23°C, sliding velocity = 1.7 mm·s⁻¹, radius of curvature of 440C pin = 127 mm, radius of sapphire ball = 3.17 mm)

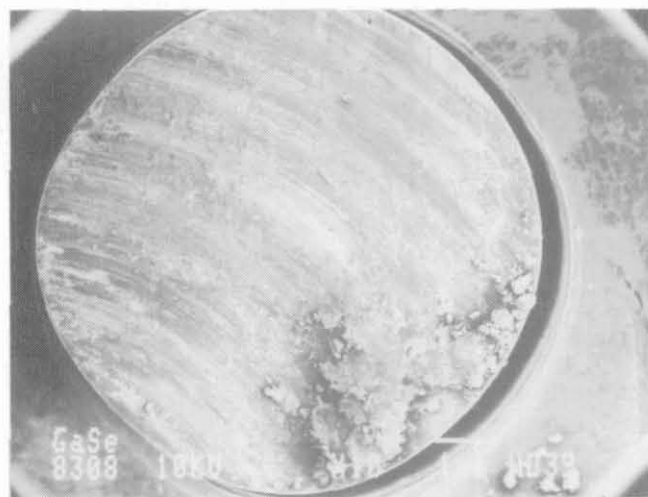
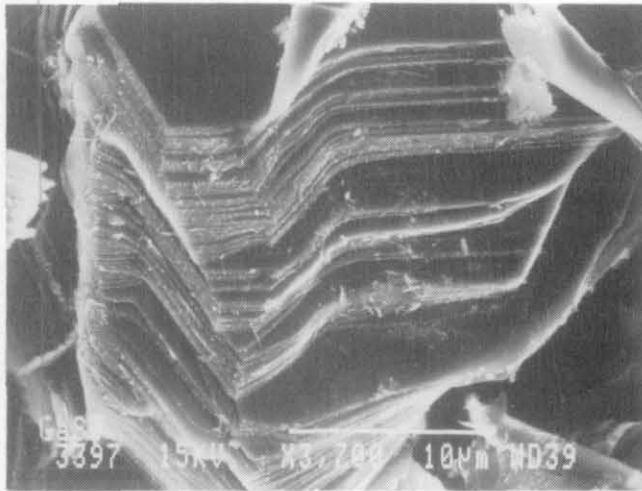
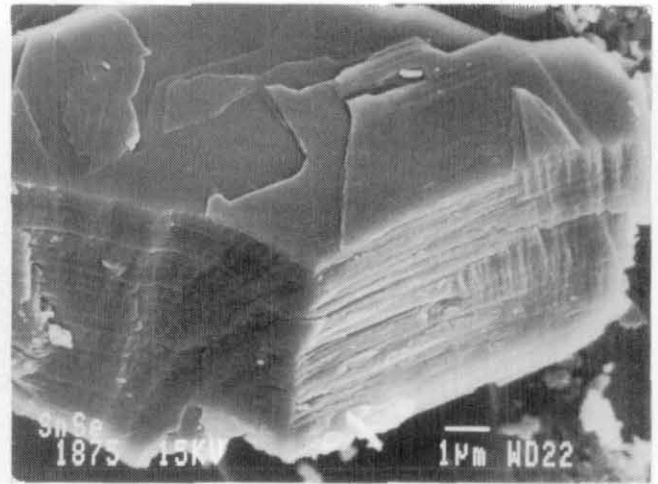


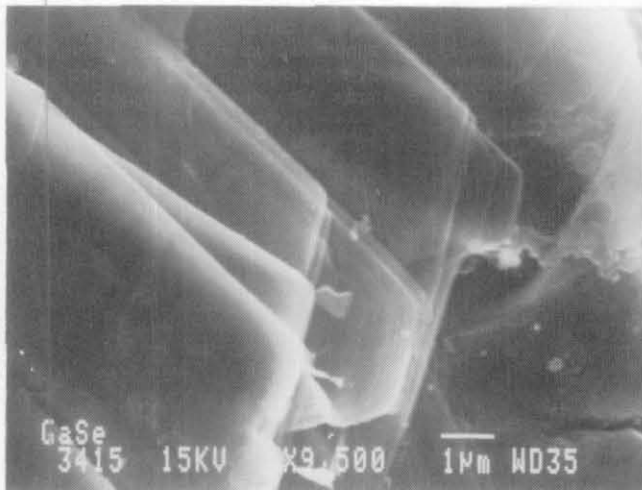
Fig. 7—SEM micrograph of transfer layer formed on a 440C pin surface during sliding against GaSe-lubricated 440C disk (load = 2N, temperature = 23°C, sliding velocity = 5 mm·s⁻¹, relative humidity = 14 percent, radius of curvature of 440C pin, 127 mm).



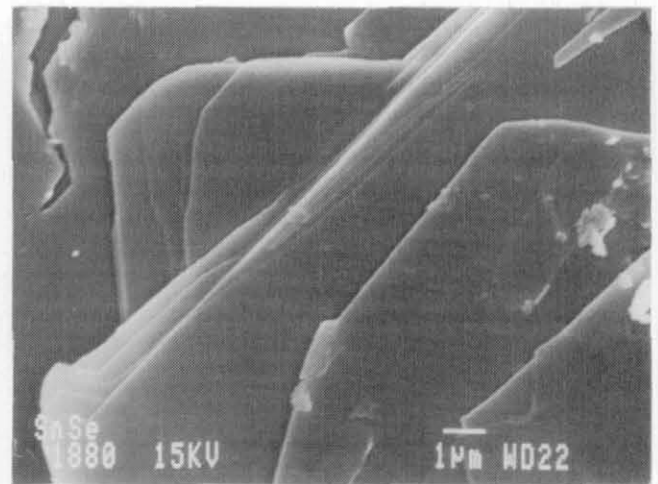
(a)



(a)



(b)



(b)

Fig. 8—SEM micrographs, showing platelike nature of GaSe and some evidence of intercrystallite slip between platelike crystallites.

- (a) free standing GaSe particles
(b) friction tested GaSe particles

Fig. 9—SEM micrographs, revealing platelike nature of SnSe and some evidence of intercrystallite slip between platelike crystallites.

- (a) free-standing SnSe particles
(b) friction tested SnSe particles

ceivable that the platelike crystallites in Figs. 8(a) and 9(a) align themselves parallel to the direction of relative motion under frictional traction. Once so aligned, they can slide over one another with relative ease to provide the level of friction coefficients shown in Figs. 5 and 6. The SEM micrographs in Figs. 8(b) and 9(b) appear to support this interpretation by revealing some microfeatures indicative of intercrystallite slip possibly due to frictional traction at sliding interfaces.

CONCLUSIONS

1. Under the test conditions of this study, it was found that low friction coefficients can be attained on tribological surfaces through the use of GaSe and SnSe.
2. The crystal chemistry of GaSe is similar to that of MoS₂. Coalescence of the pairs of mutually bonded Ga atoms in the GaSe crystal structure produces an

MoS₂ structure. Under the test conditions explored, the friction coefficients of sliding interfaces that include MoS₂ and GaSe are rather comparable.

3. Despite its layered structure, SnSe is not as lubricious as MoS₂ or GaSe. This may have been due to the fact that in the crystal structure of SnSe, adjacent layers are bound to each other with a combination of van der Waals and long-range electrostatic attractions, whereas in MoS₂ and GaSe crystals, the interlayer attraction was primarily of the van der Waals type.
4. Fundamentally, it is hypothesized that the solid lubricating capabilities and lubrication mechanisms of monochalcogenides GaSe and SnSe are primarily governed by their crystal chemistry and interlayer bonding. It is proposed that, during sliding tests, the layers can align themselves parallel to the direction of sliding motion; once so aligned, they can easily shear and slide over one another (because of the weak bonding between

layers) and thus provide low friction. In support of this proposed mechanism, electron microscopy revealed some microfeatures indicative of intercrystallite slip possibly caused by frictional traction at the sliding interface.

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