cm^{-1} (Br), and 153 cm^{-1} (I). Similarly, bands for $(C_6H_5)_4Ga_2X_2$ (X = Cl, Br, I) occur at 263 cm^{-1} (Cl), 181 cm^{-1} (Br), and 150 cm^{-1} (I). Consequently, ν_2 is assigned to the band at 320 cm^{-1} for $H_2Ga_2Cl_4$, 311 cm^{-1} for $(CH_3)_2Ga_2Cl_4$, and 330 cm^{-1} for Ga_2Cl_6.[12–16] The vibrational mode ν_3 is also dependent on the nature of the bridging and terminal groups in dimeric structures. Assignments for ν_3 are 167 cm^{-1} (Ga_2Cl_6),[12–16] 140 and 133 cm^{-1} ($(C_6H_5)_2Ga_2Cl_4$),[11] 165 and 132 cm^{-1} ($(CH_3)_2Ga_2Cl_4$), and 160 and 148 cm^{-1} ($H_2Ga_2Cl_4$). In conclusion, all spectroscopic data are fully consistent with a dimeric structure involving bridging chlorine atoms for $H_2Ga_2Cl_4$.

An attempt was made to differentiate the cis and trans isomers of $H_2Ga_2Cl_4$ by variable-temperature ^{1}H NMR spectroscopy. However, the broadness of the single observed line prevented isomer identification. The increased broadness of the line with increased temperature is consistent with the high spin and quadrupole moments of the two gallium isotopes.

All data are consistent with the hypothesis that $H_2Ga_2Cl_4$ has a chlorine-bridged dimeric skeleton. Thus, when there is a choice between hydrogen and chlorine as bridging atoms, beryllium, magnesium, and boron have bridging hydrogen; gallium has bridging chlorine. The preference of gallium for chlorine bridges may be attributed to several factors. The greater bond energy for the gallium–chlorine bond would favor chlorine bridges. The longer gallium–chlorine bonds will also minimize repulsions between gallium atoms. Furthermore, internuclear and interelectronic repulsion terms will be greater for bridged bonds than terminal bonds, thus making the weak gallium–hydrogen bond even weaker, if it is in a bridging position. Consequently, chlorine bridges are favored in gallium chemistry. Since the other elements have more stable bonds to hydrogen, hydrogen bridges with their greater angular variation can be accommodated.

Experimental Section

Materials. All compounds described in this investigation were manipulated in a standard vacuum system. The stopcocks were lubricated with Halocarbon 25-5S grease, which is not reactive to gallium(III)–chlorine compounds. The solvents were dried by conventional means. The reagents were purified by sublimation and/or fractionation. The gallanes[9] $H_2Ga_2Cl_4$ and $D_2Ga_2Cl_4$ were prepared by reacting 1 mol of $GaCl_3$ with 1 mol of $HSi(CH_3)_3$ or $DSi(CH_3)_3$ at −23 °C for 8 h. The $DSi(CH_3)_3$ was prepared by reacting $ClSi(CH_3)_3$ with $LiAlD_4$ and dry dibutyl ether at 0 °C and purified by trap to trap fractionation. Its purity was confirmed by spectroscopy and vapor pressure measurements. The compound $HGaBr_2$ was prepared from $GaBr_3$ and $HSi(CH_3)_3$ by the analogous procedure but it was observed to be significantly more unstable at room temperature than $H_2Ga_2Cl_4$.

Methylgallium dichloride,[17] $(CH_3)_2Ga_2Cl_4$, was synthesized by reacting equimolar quantities of $GaCl_3$ and $Si(CH_3)_4$ in benzene at 35 °C for 4 h.

Analyses. Gallium was determined by EDTA titration.[18] Chlorine was determined by standard gravimetric procedures. Hydrogen was measured after acid hydrolysis with a Toepler pump–gas buret assembly. Anal. Calcd for $H_2Ga_2Cl_4$: Ga, 49.2; Cl, 50.1; H, 0.71. Found: Ga, 49.3; Cl, 50.0; H, 0.68. Calcd for $D_2Ga_2Cl_4$: Ga, 48.9; Cl, 49.7. Found: Ga, 48.9; Cl, 49.8.

Infrared Spectra. The infrared spectra were recorded in the range 4000–250 cm^{-1} by using a Perkin-Elmer Model 457 spectrometer. Condensed-phase spectra were observed by using a low-temperature cell[19] equipped with KBr optics. The sample was cooled by a cold finger which contained liquid nitrogen.

Raman Spectra. The Raman spectra were recorded by using a Spex Model 14018 double monochromator instrument and the 5145- or 4880-Å line of a coherent radiation argon ion laser. Spectra were observed when the sample was cooled to 120 K. Direct-current detection was employed. Band positions were measured relative to the laser line and should be accurate to ±1 cm^{-1}.

The IR spectra are as follows [frequency, cm^{-1} (intensity: vs, very strong; s, strong; m, medium, w, weak; sh, shoulder)]. $H_2Ga_2Cl_4$: 2051 (vs), 581 (vs), 338 (s), 320 (m), 202 (m), 160 (m), 148 (m), 136 (m), 114 (m), 105 (m), 52 (vs). $D_2Ga_2Cl_4$: 1468 (vs), 419 (vs), 383 (s), 321 (m), 314 (m), 202 (m), 160 (m), 148 (m), 135 (m), 112 (m), 103 (m), 52 (vs).

Nuclear Magnetic Resonance Spectra. The ^{1}H NMR spectra were recorded at 100 MHz by using the Varian XL-100 spectrometer equipped with variable-temperature capability. The solvent for the 25% solution of $H_2Ga_2Cl_4$ was toluene-d_8. Tetramethylsilane was used as internal reference. The following are the temperature (°C), chemical shift (δ ppm), and width of line at half-height (Hz): −10, 4.06, 64; −60, 4.58, 22; −80, 4.86, 21.

Acknowledgment. This work was supported in part by the Office of Naval Research. We also wish to thank Professors P. Prasad of this department and T. B. Brill, University of Delaware, for the Raman spectral data. The XL-100 NMR spectrometer was obtained by a grant from the National Science Foundation.

Registry No. $H_2Ga_2Cl_4$, 72214-14-3; $D_2Ga_2Cl_4$, 72214-15-4.

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Contribution from the Laboratoire des Acides Minéraux,
L.A. 79, Université des Sciences et Techniques du Languedoc,
34060 Montpellier Cédex, France

Ionic Species in HF–SbF$_5$ Solutions. An Infrared Spectroscopy Investigation

B. Bonnet* and G. Mascherpa

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Infrared spectra of HF–SbF_5 solutions were measured previously by Hyman et al.[1] More recently, Couzi et al.[2] reported the infrared spectra of a crystalline solid at 77 K, formulated as $H_2F^+SbF_6^-$. However, these results have been criticized by Christe et al.,[3] who suggested that this compound should be better formulated as $SbF_5{\cdot}HF{\cdot}H_2O$.

In a previous paper[4] we reported the phase diagram of the HF–SbF_5 system and confirmed the existence of the $2HF{\cdot}SbF_5$ adduct postulated by Couzi and co-workers. However, the infrared spectra given by Couzi et al. for HF–SbF_5 solutions presented some features, not easily reconcilable with the earlier data of Hyman and co-workers. Further, Gillespie and Moss[5] have conclusively shown from electrical conductivity and NMR measurements that polymeric anions such as $Sb_2F_{11}^-$ are present in solution even at relatively low concentration in SbF_5 (below 22 mol % of SbF_5, which is significantly lower than the 33.33 mol % of SbF_5 concentration for $H_2F^+SbF_6^-$). This leads to the suggestion that cationic species also could be solvated, giving rise to the $H_3F_2^+$ ion, analogous to the $H_5O_2^+$ grouping which has been recently shown by Zundel and co-workers[6] to play a major role in aqueous solutions of strong

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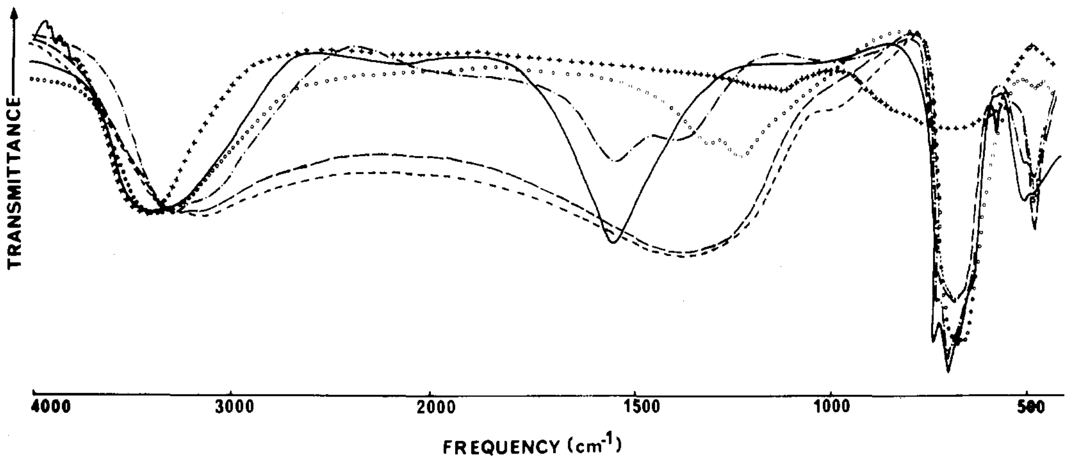

Figure 1. Infrared spectra of HF–SbF_5 solutions (mol % of SbF_5: 85 (—), 50 (-•-), 40 (--), 33.3 (---), 20 (OOO), liquid HF (+++)).

acids. Thus, there is considerable disagreement among previous workers about the nature of the ionic species in the HF–SbF_5 system, and, in order to understand the vibrational spectra of these solutions, we decided that a new investigation of the infrared spectra of HF–SbF_5 solutions was necessary.

Experimental Section

Hydrogen fluoride (Merck-Schuchardt, 0.04% water content) was stored over niobium pentafluoride and purified by trap to trap distillation in a Kel-F vacuum system. The deuterium fluoride was prepared by the reaction of D_2SO_4 with previously dried CaF_2 at 150 °C. Antimony pentafluoride was obtained from the Allied Chemical Co. and bidistilled for purification.

All preparations, storages, and transfers were carried out in Kel-F vessels, similar to those described by Hyman and co-workers. Unlike previous observations of these authors, no attack on AgCl windows was observed. However, in some cases, a white film appeared on the windows, resulting from superficial hydration of the solutions.[7] After removal of volatile material, in vacuo, the infrared spectrum of the film appeared to be that of $SbF_5 \cdot HF \cdot H_2O$.[3] Infrared spectra were recorded with a Perkin-Elmer spectrometer, Model 180.

Results and Discussion

Infrared spectra of HF–SbF_5 solutions with different concentrations are presented in Figure 1. These experimental data are in very close agreement with previous results of Hyman and co-workers.[1] Bands above 800 cm^{-1} are shifted upon hydrogen–deuterium substitution, and therefore two separate frequency ranges of interest will be discussed. In the 4000–800-cm^{-1} range, the bands observed correspond to the vibrational modes of protonated HF species; bands in the 800–400-cm^{-1} range are characteristic of Sb–F vibrational modes of anionic species present in solution. Detailed spectra of HF–SbF_5 solutions and those of solid SbF_5 and the crystalline solids $CsSbF_6$ and $CsSb_2F_{11}$ are given in Figure 2 for comparison.

Anionic Species in HF–SbF_5 Solutions. For dilute SbF_5 solutions (0–20 mol % SbF_5), the infrared spectra between 1000 and 400 cm^{-1} show only a very intense single band at about 660 cm^{-1}, characteristic of the SbF_6^- ion.[8-11] This observation is in agreement with Gillespie and Moss'[5] data which show that SbF_6^- anions are predominant below 22%.

Numerous infrared and Raman spectra have been reported for salts containing the undecafluorodiantimonate anions,[12,13] but complete data on simple salts such as $CsSb_2F_{11}$ are lacking.[14] However a comparison can be made in Figure 2 with the infrared spectrum of $CsSb_2F_{11}$. The sharp and relatively intense band at 480 cm^{-1}, in a region free of absorption in the SbF_6^- spectrum, is assigned to the Sb–F–Sb bridge[15,16] stretching. An additional effect of polymerization is the broadening of the absorption of terminal Sb–F stretching vibrations at 700 cm^{-1}, which is more structured on the high-frequency wing. In the 1000–400-cm^{-1} range, spectra of $HF \cdot SbF_5$ solutions containing 20–40 mol % SbF_5 are very similar to that of solid $CsSb_2F_{11}$, in particular with respect to the 490-cm^{-1} band which is characteristic of the Sb–F–Sb

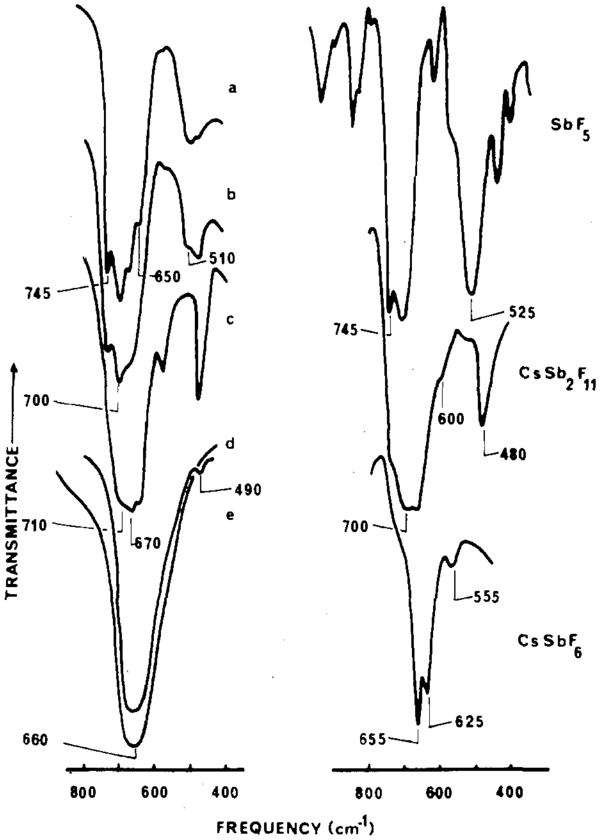

Figure 2. Vibrational infrared spectra of anions in HF–SbF_5 solutions (mol % of SbF_5: 85 (a), 50 (b), 40 (c), 20 (d), 10 (e)) compared to those of SbF_5, $CsSb_2F_{11}$, $CsSbF_6$, in the solid state.

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bridge. This absorption reaches its maximum for a 40% solution.

Although higher polymeric anions such as $Sb_3F_{16}^-$ or $Sb_4F_{21}^-$ are known in the solid state or in solution,[17,18] unfortunately, detailed infrared spectra are not available in the literature for comparison. We may reasonably assume that, with increasing polymerization, the infrared spectrum of the anionic chain should become closer to that of liquid SbF_5. For concentrations above 40 mol % SbF_5, the IR spectra are very close to that of SbF_5. In particular, a new absorption is observed at about 520 cm^{-1}, which is also found in the SbF_5 spectrum. In addition, the absorption of the terminal Sb–F stretching vibrations becomes more structured on the high-frequency wing. This indicates the formation of highly polymerized anions $[Sb_nF_{5n+1}^-]$.

Cationic Species. Solutions at concentrations between 100 and 85% SbF_5 show a very simple spectrum. The broad absorption at about 3360 cm^{-1} and the intense band at 1565 cm^{-1} are highly reminiscent of the infrared spectrum of liquid water and suggest the existence of the triatomic entity H_2F^+. This cation has already been postulated in the $2HF{\cdot}SbF_5$ compound by Couzi et al.,[2] who have proposed a complete assignment of the infrared spectrum of H_2F^+. Our results are markedly different, particularly with regard to the frequency and profile of the broad absorption band at 1565 cm^{-1}. However, we can propose similar assignments based on the close resemblance of our spectra with that of liquid water; the 3360-cm^{-1} absorption arises from ν(F–H) stretching vibrations and the 1565-cm^{-1} band from the δ(HFH) bending vibration. Since the polarity of the HF bond increases on protonation, the stretching modes ν(F–H) are observed at 3360 cm^{-1}, lower than the frequency of the corresponding modes in liquid HF.[19]

In the range 85–40% SbF_5, at increasing concentration of HF, the intensities of characteristic bands of H_2F^+ decrease progressively. This is clearly observed for the bending vibration at 1565 cm^{-1} which occurs in a frequency range not obscured by other interfering bands. A new broad absorption is observed at 1390 cm^{-1}, and these changes must be related to the solvation of H_2F^+ species. The H_2F^+ bending vibration totally disappears at about 40 mol % SbF_5, which indicates that all the H_2F^+ cations have been solvated. This can be correlated to the spectral evolution in the anionic vibration range, which indicates the disappearance of polymeric species higher than $Sb_2F_{11}^-$. Therefore at this 40% concentration, the H^+/HF ratio should be close to 1/2. The 1390-cm^{-1} absorption is thus to be related to a new species in solution, and *the most probable candidate is the $H_3F_2^+$ ion.* This ion can be alternatively considered either as the monosolvated fluoronium ion $H_2F^+{\cdot}HF$ or as the disolvated proton $[HF{\cdot}H{\cdot}FH]^+$. The $H_3F_2^+$ ion has been studied by ab initio method by Diercksen, Niessen, and Kraemer.[20] They have shown that, at the equilibrium geometry, this ion has a single-minimum potential energy curve for the central proton with a F···F separation of 2.27 Å. This F···F distance is close to the F···F distance in hydrogen bifluoride ion, HF_2^-, for which there is strong experimental evidence of a centered proton[21] (however Williams and Schneemeyer[22] have pointed out the influence of strong lattice effects on HF_2^- ion geometry).

On the assumption that $H_3F_2^+$ ion retains the same geometry in solution, in the IR spectrum, the band attributed to the stretching motion of the central hydrogen–fluorine bonds should present some similarities with that of HF_2^- ion. The broad absorption at 1390 cm^{-1} is remarkably similar to the ν_3 absorption in the HF_2^- spectrum[21] and, therefore, should be assigned to the asymmetric stretching vibration of the F–H–F bridge.

Spectra of solutions in the 40–20% SbF_5 range are strongly reminiscent of those of concentrated aqueous solutions of strong acids, in particular with respect to the continuous absorption culminating at about 1370 cm^{-1}. Recently, Zundel and co-workers[6] and Sokolov and co-workers[23] have emphasized the role of the diaquated proton $[H_2O{\cdot}H{\cdot}OH_2]^+$ in acid solutions, and it seems probable that the hydrogen dihydrofluoride ion plays a similar role in superacid solutions. *The fact that the 1565-cm^{-1} absorption is not observed below 40% SbF_5 indicates that the H_2F^+ ion no longer vibrates as an entity in solution and the excess proton is delocalized between the two HF molecules.* It should be noted that the identification of H_3O^+ or $H_5O_2^+$ species in aqueous solutions of strong acids by infrared spectroscopy is still controversial,[6,24,25] due to the near coincidence of the bending vibration of H_3O^+ and of terminal water molecules of $H_5O_2^+$. As for HF–SbF_5 solutions, H_2F^+ and $H_3F_2^+$ ions exhibit very different spectra in the range 3000–1000 cm^{-1}, and distinction between the two species appears possible.

Below 20% SbF_5 the continuous absorption associated with the $H_3F_2^+$ group decreases, and in the range 1300–700 cm^{-1}, solution spectra are obscured by the intense absorption of librational modes of HF molecules in the chains and their overtones, giving a maximum of absorption below 1300 cm^{-1}. With increasing HF concentration the vibrations of the HF molecules shift toward the position in which they are found in pure liquid HF.[19] The maximum in the terminal ν(F–H) range is shifted to 3450 cm^{-1}, and the frequencies of the librational modes are observed between 800 and 600 cm^{-1}.

Conclusion

We have shown in this study that the $H_3F_2^+$ and solvated $H_3F_2^+$ ions are the predominant cationic species over a large concentration range (0–40 mol % of SbF_5) in the HF–SbF_5 system. The observed frequency of 1390 cm^{-1} for the antisymmetric stretching motion of the central FHF group of the $H_3F_2^+$ ion indicates that the F–H–F bond length is similar to that of the hydrogen bifluoride ion. This observation is in agreement with the F···F distance of 2.27 Å obtained by the ab initio study of Diercksen et al. If the proton is centered in the hydrogen bond, a F–H distance of 1.13 Å should be expected. It is of course impossible from our data to prove the existence of a centered H atom in the $H_3F_2^+$ species. However, the very low frequency assigned to ν_{as}(FHF) might be related to an important lengthening of the F–H distance compared to F–H ($\simeq$0.92 Å) in gaseous HF.

The fluoronium ion, H_2F^+, is observed only in concentrated solutions in SbF_5 (40–100%) with highly polymerized and weakly basic counterions. This is in contradiction with the widespread assumption that H_2F^+ is the only protonated species in $HF{\cdot}SbF_5$ solutions. Particularly, at the concentration ratio 2:1 ($2HF{\cdot}SbF_5$) the ionic species $H_3F_2^+(HF)$ and $Sb_2F_{11}^-$ are found predominantly instead of the H_2F^+ and SbF_6^- ions.[2,5]

However, recent studies[26-28] are more consistent with our results. Hogeveen,[27] on the basis of kinetic measurements,

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shows that, in the HF–SbF_5 system, the rate of protonation increases more rapidly than linearly with the excess SbF_5. Furthermore, Brouwer and co-workers,[28] on the basis of kinetic measurements and studies of mechanisms of protonation, have proposed an acidity scale in which the $HF \cdot SbF_5$ solution is more acidic than the $9HF \cdot SbF_5$ mixture. These observations are in agreement with our findings since we have shown that addition of SbF_5 leads quickly to the depolymerization of the protonated HF chains and that the most acidic entities $H_3F_2^+$ and H_2F^+ are formed in HF–SbF_5 solutions with concentration above 40 mol % in SbF_5. These ions may therefore play a similar role to that of $H_5O_2^+$ and H_3O^+ species in aqueous acid solutions.

Acknowledgment. We thank Dr. J. Rozière of Université des Sciences et Techniques du Languedoc for helpful discussions.

Registry No. HF, 7664-39-3; SbF_5, 7783-70-2; $H_3F_2^+$, 72258-82-3; $CsSb_2F_{11}$, 23751-61-3; $CsSbF_6$, 16949-12-5.

Contribution from the Baker Laboratory of Chemistry,
Cornell University, Ithaca, New York 14853

Effect of Chalcogen Nonstoichiometry on Superconductivity in Chevrel-Phase Tin Molybdenum Sulfides[1]

Frank S. Delk, II, and M. J. Sienko*

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The ternary molybdenum chalcogenides, $M_xMo_6X_8$ (M = Pb, Sn, rare earth elements; X = S, Se), usually called Chevrel phases,[2] are of special interest because of high superconducting critical temperatures,[3] high critical fields,[4] and coexistence of magnetic order and superconductivity.[5] Unfortunately, the materials are almost never prepared pure, and there are numerous discrepancies in the literature arising from failure to control stoichiometry. Not only is the content of ternary element M variable but also the ratio of molybdenum to chalcogen can be made greater than the ideal 6/8 value.

As part of a continuing program to investigate the chemical control of superconductivity, we have recently examined a large body of data on Chevrel phases to discover, if possible, the reason for the wide variability in reported parameters. Even for a single phase, e.g., $PbMo_6S_8$, reported T_c's ranged from 9.8 to 14.7 K. We found that T_c is a very sensitive function of the lattice parameters. Indeed, when the materials were grouped according to the formal charge on the ternary element M, T_c turned out to be a linear function of the hexagonal crystallographic c/a ratio.[6] In this communication, we report the result of a deliberate effort to enhance the superconducting critical temperature of $SnMo_6S_8$ by driving it off stoichiometry and thereby raising its c/a ratio.

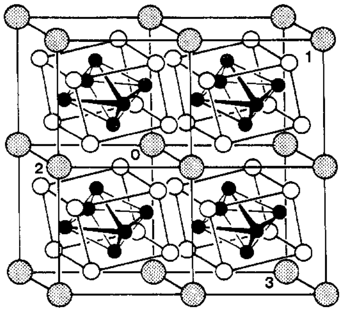

Figure 1. Idealized version of $SnMo_6S_8$ structure: black circles, Mo; white circles, sulfur; shaded circles, Sn.

Experimental Section

Preparation of Samples. Samples of $SnMo_6S_{8-x}$ were prepared by direct synthesis from ultrapure starting elements: Sn (99.999 95%, from Alfa Division, Ventron Corp.), Mo (99.95%, from United Mineral and Chemical Corp.), and S (99.9999%, from Atomergic Chemetals Corp.). The molybdenum powder was treated with hydrogen for 24 h at 1000 °C and stored in a helium Dri-Lab until needed. Amounts of elements appropriate for forming a series of materials with x = 0, 0.5, 1.0, 1.5, and 2.0 were weighed into silica tubes and the tubes degassed to 10^{-6} torr and then sealed. The tubes were wrapped in heavy Kanthal wire and heated together in a box furnace. Furnace temperature was slowly raised to 1000 °C over the course of 7 days, allowing the molybdenum and sulfur to prereact without thermal runaway. After 24 h at 1000 °C, the sample tubes were quenched in air and vigorously shaken to homogenize the sample. They were immediately reheated to 1200 °C, left to react for 24 h, and then air quenched.

Powder X-ray Diffraction. X-ray diffraction photographs were made by using a 114.6-mm diameter Debye–Scherrer camera with nickel-filtered copper Kα radiation. Line positions were measured with a precision better than 0.05 mm. Intensities were estimated visually. Angles and d spacings were calculated by the Straumanis method, correcting for film shrinkage and camera radius uncertainty. Lines were assigned hkl indices with aid of a Fortran program that calculated line positions and intensities from single-crystal data. Because Chevrel-phase X-ray patterns typically show hundreds of lines, many of which are uniformly weak (especially for $\theta_{hkl} > 30°$), an iterative procedure was used. Well-resolved lines in the front reflection region were indexed and used to calculate an initial set of lattice parameters. These new lattice parameters were used to generate line positions for the 120 most intense reflections. Increasing θ_{hkl} were indexed, and the process was repeated until all lines were identified. Final lattice parameters and errors were calculated by using Cohen's least-squares fitting for indexed lines between 30 and 90°.

Superconducting Transition Determination. Onset of superconductivity was measured by Meissner Flux expulsion by using an apparatus described elsewhere.[7] The detection system is a primary coil with two opposed external secondary coils wound symmetrically about it. The sample sits in one of the secondary coils and transition to the superconducting state is seen as a large off-null signal. Temperature was measured with a calibrated germanium resistance thermometer from CryoCal, which was checked against the boiling point of helium and the transition temperatures of lead and niobium. T_c was taken as the temperature at which the inductive transition was half complete. The width of the transition was taken as the difference between the temperature at which the transition was 10% complete and the temperature at which it was 90% complete.

Results and Discussion

The Chevrel phases are usually rhombohedral and crystallize in the space group $R\bar{3}$. As shown in Figure 1, which is an idealized version of $SnMo_6S_8$, the central feature of the structure is the Mo_6S_8 unit, which can be visualized as an octahedron of molybdenum atoms with each triangular face of the octahedron capped by a sulfur atom. The quasi-cubic unit Mo_6S_8 is located in a nearly cubic array of the ternary atoms Sn, except that the Mo_6S_8 unit is rotated ~20° about

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