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Superconductivity in Alkaline Earth Metal and Yb Intercalated Group VI Layered Dichalcogenides

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Alkaline earth metals and Yb have been intercalated into Group VI layered dichalcogenides, e.g., MoS_2, etc., by the liquid ammonia method at low temperatures. Chemical analysis and X-ray data indicate that ammonia is also intercalated along with the metal and that the c axis increases by ~3 Å in all the intercalated materials. In most cases, these compounds are only partially intercalated in that some pure unintercalated phase is present.

Superconductivity has been observed in these intercalated compounds with the highest value T_{onset} of 5.7°K for $Ba_x(NH_3)_yMoS_2$; the T_{onset} temperatures depend on the nature of the metal and the host dichalcogenides but not on the concentration of the intercalated metal ion. Fine-particle (1–10 μm size) materials which are fully intercalated do not exhibit the superconductivity behavior as measured by the ac susceptibility method. The results are discussed in terms of the current band models for the Group VI MCh_2 materials and compared with alkali metal intercalated MoS_2 as reported by Somoano et al. (*4*).

Introduction

The layered transition metal dichalcogenides, because of their unique structure, show a variety of interesting properties, one of which is that they can be intercalated with organic molecules or metal ions. [For extensive reviews on the physical properties of the layered dichalcogenides see Hulliger (*1*) and Wilson and Yoffe (*2*)]. Such intercalations are known to cause significant changes in the physical properties of the host MCh_2 (M = transition metal; Ch = chalcogen) layer material. For example, the semiconductors MoS_2, ZrS_2, and HfS_2 become superconducting when intercalated with alkali metals [Somoano and Rembaum (*3*, *4*) and Barz et al. (*5*)]. In this paper we report on alkaline earth and divalent rare earth intercalation in MoS_2 and other Group VI dichalcogenides and on the superconductivity of these materials.

Experimental and Results

The starting materials were both powder and single-crystal MoS_2. The powders were prepared by direct reaction of the elements at ~900°C and the crystals by halide vapor transport growth from prereacted powders. All the MCh_2 materials were characterized by X-rays, and the hexagonal lattice parameters agreed with the values reported in the literature (*2*). Since the alkaline earth and the divalent rare earth metals dissolve in liquid ammonia (*6*) to give the characteristic blue solution due to solvated electrons, we were able to intercalate our materials by "reacting" them with the blue metal–ammonia solution.

Weighed amounts of the materials, i.e., MCh_2 plus the metal to be intercalated, were introduced into a reaction flask where freshly distilled NH_3 was condensed. Reaction was carried out at −40°C with times ranging from a few hours to several days. The apparent slowness of the intercalation is consistent with the considerable decrease in the volume and entropy of the system associated with the incorporation of the intercalate species into the chalcogenide lattice. The solution was kept dilute with respect to the metal, since at higher concentrations (and at higher temperatures) there is a tendency for the formation of the metal amide (*7*, *8*). The reaction was considered complete when the solution became colorless; the product was then recovered after vacuum

TABLE I

Chemical, Crystallographic, and Superconductivity Data on Intercalated MCh_2 Compounds

Starting composition A_xMCh_2[a]	Composition from analysis per MCh_2[b]	% Intercalation[c]	Hexagonal C parameter[d] (Å)	δ (Å)	T_c (°K)
MoS_2 (2*s*)	—	—	3 × 6.15	—	—
MoS_2 (3*s*)	—	—	3 × 6.13	—	—
$Sr_xMoS_2(3s)$					
x 0.01	—	5	3 × 9.30	3.17	5.1
0.05	—	10	3 × 9.30	3.17	5.2
0.1	$Sr_{0.04}(NH_3)_{0.17}$	40	3 × 9.30	3.17	—
0.2	$Sr_{0.05}(NH_3)_{0.01}$	40	3 × 9.30	3.17	5.1
0.3	$Sr_{0.17}(NH_3)_{0.4}$	50	3 × 9.30	3.17	4.9
0.36	$Sr_{0.14}(NH_3)_{0.42}$	50	3 × 9.30	3.17	5.1
0.5	$Sr_{0.19}(NH_3)_{0.54}$	60	3 × 9.30	3.17	5.2
1.0 (117 μm powder)	$Sr_{0.73}(NH_3)_{0.99}$	90	3 × 9.30	3.17	5.0
1.0 (53 μm powder)	$Sr_{0.68}(NH_3)_{1.27}$	95	3 × 9.30	3.17	5.0
1.0[e] (<10 μm powder)	—	40	3 × 9.30	3.17	—
1.20[e] (<10 μm powder)	$Sr_{0.97}(NH_3)_{1.62}$	50	3 × 9.30	3.17	—
0.2 (ceramic)	—	25	3 × 7.19	1.06	—
0.2 (MoS_2, 2*s*)	—	65	2 × 9.35	3.2	5.0
$A_xMoS_2(3s)$					
0.2 Ca	—	70	3 × 9.23	3.10	3.6
0.2 Ba	—	15	3 × 9.36	3.23	5.7
0.2 Yb	$Yb_{0.10}(NH_3)_{0.16}$	30	3 × 9.21	3.08	2.4
1.0 Yb[e] (<10 μm powder)	—	100	3 × 9.21	3.08	—
$Sr_xMoSe_2(2s)$					
0.0	—	—	2 × 6.46	—	—
0.2	—	60	2 × 9.65	3.19	5.0
$A_xWS_2(2s)$					
0.0	—	—	2 × 6.18	—	—
0.2 Sr	—	40	2 × 9.35	3.17	3.5
0.4 Yb	—	95	2 × 9.30	3.12	2.2
$Sr_xWSe_2(2s)$					
0.0	—	—	2 × 6.49	—	—
0.2	—	40	2 × 9.76	3.27	1.4[f]
$Sr_xTaS_2(2s)$					
0.0	—	—	2 × 6.05	—	0.8
0.2	—	100	2 × 9.15	3.1	2.8

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[a] Crushed single crystals of MCh_2 unless otherwise stated.

[b] The analysis pertains to the total bulk sample which is partially intercalated, and, hence, the relative concentration of Sr in the intercalated regions is greater.

[c] Obtained from the intercalated and unintercalated (00*l*) peak intensities (Cu*Kα*; 35 kV; 15 mA).

[d] On intercalation, the *a* axis expands by negligible amount (~0.02 Å) compared to c, indicating that the Ch–M–Ch slabs remain intact.

[e] These intercalated products did not exhibit superconductivity (see text).

[f] Not clear.

evaporation of the ammonia. Since the samples are sensitive to air and moisture, subsequent handling was done in dry N_2 atmosphere. The compounds were analyzed for the alkaline earth metal (e.g., Sr) and ammonia by standard methods, and it was found that the Sr concentration in the samples was always less than the starting composition of the Sr in solution. This might be due to slight decomposition of the Sr–NH_3 solution to form $Sr(NH_2)_2$ which does not intercalate into MoS_2 at low temperatures.[1] Chemical analysis indicated that ammonia is also intercalated into MCh_2 along with the divalent metals; the analysis data (see Table I) suggests an overall composition $A_x(NH_3)_yMCh_2$ (A = alkaline earth metal or Yb; $x \gtrsim y$). The ammonia analysis may not be very representative in the sense that some adsorbed ammonia on the intercalated product could also be contributing to the total value. Additional evidence for ammonia intercalation along with the A metal comes from X-ray data (see below). X-ray analyses (made with Cu$K\alpha$ radiation) indicate that in most cases the materials are not completely intercalated in the sense that a pure MCh_2 phase is always seen along with the intercalated phase. This is especially evident at low concentrations of the A metal when large-particle-size (crushed single crystals) MCh_2 is used as the starting material. As determined by X-ray line intensities, the relative concentration of the intercalated product could be increased with higher initial compositions of the A metals. We have been able to prepare completely intercalated products by the proper choice of the particle size (<1–10 μm) of MCh_2 materials and concentration of the A metal. Partial intercalation of the MoS_2 samples was also noted by Somoano and Rembaum (*4*) on the Na and K intercalated MoS_2 samples, and it is clear that the differences in the degree of intercalation are mainly of kinetic origin. The *c* lattice parameter increase per unit MCh_2, δ, of the intercalated material is ~3 Å while the *a* parameter is almost unaffected (Table I). Also, δ does not depend on the concentration of the A metal in a given MCh_2 even though it differs slightly for different A ions. The fact that δ varies only between 3.1–3.2 Å in all the A_xMCh_2 presently studied can be explained by the presence of ammonia intercalated along with the metal since its diameter (~3 Å) is only slightly larger than the divalent ions under consideration. X-ray data also indicate that the intercalated species (A metal plus NH_3) are present between every layer, i.e., stage I intercalation. This is the case whether the starting materials are either 2*s* or 3*s* modifications. The detailed structure and coordination of the A ion in $A_x(NH_3)_y$ MCh_2 compounds are not known at the present stage, but from the available X-ray data it appears that, at least at low concentrations, A ions and NH_3 molecules randomly occupy the octahedral (or distorted octahedral) holes in the van der Waals gap. However, we feel that the solvated A^{2+} species are to be treated as single entities rather than discrete A ions and NH_3 molecules in order to be consistent with structural considerations and chemical analysis data.

The intercalated products decompose on exposure to air and moisture within a few hours, and this can be monitored nicely by looking at the X-ray peak intensities. In a partially intercalated sample, the intercalated (00*l*) peak decreases in intensity and finally disappears, leaving only the pure MCh_2 peak which grows in intensity. This indicates that the dilated *c* axis has collapsed to the original state, leading to deintercalation. The metal is presumed to diffuse out of the lattice to give decomposition products at the surface of MCh_2. Supporting evidence for this mechanism has been obtained from scanning electron micrographs. These exposed deintercalated samples did not exhibit superconductivity. The materials are, however, stable for months in a dry N_2 atmosphere and exhibit reproducible superconductive behavior. It is worth mentioning here that in samples showing a mixture of intercalated and unintercalated phases, we observed an apparent increase in the percent of the intercalated phase (ranging from 15 to 35 %) after storing at room temperature for periods of 8–12 months. It appears that the $A_x(NH_3)_y$ species present in the intercalated regions slowly diffuse into the bulk of the unintercalated crystal, still retaining the stage I arrangement. It is remarkable that either after deintercalation or diffusion over a period of time, the X-ray peaks remain sharp, indicating that there is no disorder introduced into the crystal lattice.

We could not intercalate the Group VI MCh_2 materials with pure NH_3, consistent with the observations of Gamble et al. (*9*). On the other hand, Sr metal can be intercalated into MoS_2

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[1] In fact, we were not successful in intercalating either pure $Sr(NH_2)_2$ or ammonia into MoS_2 at low temperatures.

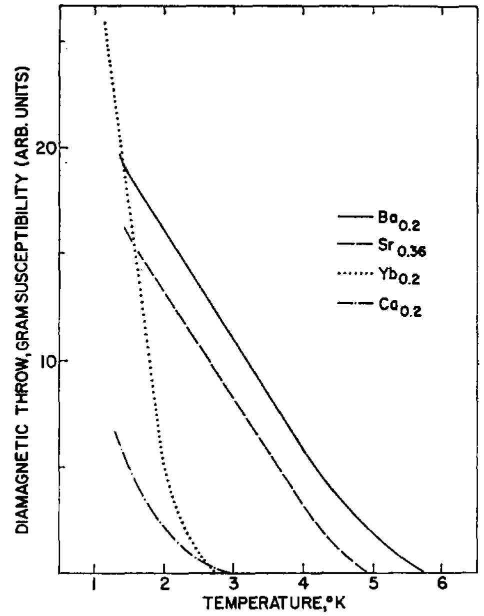

FIG. 1. Superconductive transitions of A_xMoS_2 (A = Yb, Ca, Sr, and Ba) intercalated compounds in 100 Hz ac susceptibility.

by direct reaction at high temperatures (600°C). Some SrS is formed along with intercalated material, and the *c* axis increase is smaller compared to the ammoniated products (Table I). The valence state of Sr appears to be divalent, and the compounds are also sensitive to air and moisture.

The samples were checked for superconductivity down to 1.25°K by a 100 Hz ac susceptibility method. All unintercalated MoS_2 samples showed no evidence of superconductivity, while those intercalated with Ca, Sr, Ba, and Yb became superconductors below 5.8°K. As in the case of alkali metal intercalated MoS_2 (*3*, *4*), we also observed broad, rather incomplete, transitions (Fig. 1). The onset temperatures of superconductivity (which we note as the highest temperature at which the shielding currents could first be detected) together with the data of the change of lattice spacing along the *c* axis (δ) are shown in Table I.

Discussion

We assume, as do Somoano et al. (*3*, *4*), that the normally diamagnetic semiconductor MoS_2 becomes metallic and superconducting by a transfer of electrons from the intercalated species. It is likely, based on the current band model for MoS_2 (*10–12*) which has the Fermi level lying between the filled d_{z^2} and the upper-lying empty *d* bands (probably $d_{x^2-y^2}$ and d_{xy}), that electrons are transferred to the empty bands, causing an upward shift of the Fermi level to a region of higher density of states. If we compare the onset of the superconducting transition temperatures, T_c, of the alkali and alkaline earth metal intercalated MoS_2, we find the latter to be slightly lower (~0.5–1°K) (Table I). Since they are both strong electron donors, it is unlikely that the electron transfer process is different in the two cases. The fact that the alkaline earth metals are capable of donating two electrons per metal should not so much affect the onset temperature as it would the concentration of metal required to produce the initial superconductivity. The primary difference between the alkali and the alkaline earth intercalates is that the latter have ammonia intercalated along with the metal. It may be assumed that the ammonia is bonded to the metal with the result being that the electron transfer process to the chalcogenide is slightly changed.

Although ammonia is intercalated with all alkaline earths (and Yb), the observed increase in the lattice spacing in the *c* direction (δ) is related to the size of the intercalated alkaline earth metal, i.e., Ba > Sr > Ca > Yb. As can be seen from Fig. 2 and Table I, T_c increases with increasing δ in MoS_2 intercalated products. The slight

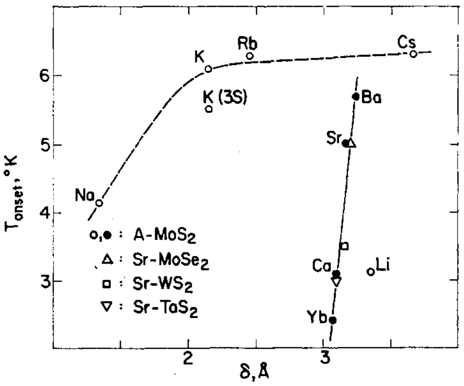

FIG. 2. Plot of T_{onset} vs δ for various intercalated MCh_2 materials. Data on the alkali metal intercalates are from Somoano et al. (*4*). Alkaline earth (and Yb) intercalated compounds (and Li–MoS_2) fall on a line of different slope due to the intercalation of ammonia along with the A metal.

but real dependence of T_c on δ which we measure has also been observed in alkali metal intercalated MoS_2 (*4*) (Fig. 2). The explanation for this is presently unclear although Somoano et al. (*3, 4*) speculate on several possible mechanisms. A significant point is that the alkali and the alkaline earths show the same behavior despite the fact that ammonia is associated with the latter! In Fig. 2, we plot δ vs the onset transition temperature, and it is seen that the alkalies which contain no ammonia fall on one curve and the alkaline earths which contain ammonia fall on another with a vastly different slope. The interesting point is that lithium falls very close to the alkaline earth curve. This suggests that the anomalous c parameter of Li intercalated MoS_2 (*4*) is a result of ammonia intercalation, and in that respect, it is similar to the alkaline earth metals (and Yb) rather than the alkali metals.

It is clear from Table I that for the system we studied in detail, i.e., Sr_xMoS_2, the superconducting onset temperature has no apparent concentration dependence. The broadness of the transition, as seen in Fig. 1, can be interpreted as being due to concentration gradients. All samples which showed superconductivity were partially intercalated in the sense that X-ray analyses always showed a mixture of the pure MoS_2 phase and a single intercalation phase. As the concentration of the strontium is increased in the ammonia solution, the percent of the intercalated phase increases relative to pure MoS_2 but with no corresponding increase in the lattice parameter. This behavior indicates that in the process of intercalation, where the metal–ammonia solution is in contact with an MoS_2 particle, the layers in certain regions of a crystallite are separated and subsequently filled by metals plus ammonia at an "optimum concentration" to produce regions in the crystallite which have the highest transition temperatures in the system. This does not necessarily mean that this "optimum concentration" is one where the intercalation is a maximum, i.e., where the maximum number of electrons are transferred to the MoS_2 bands. In fact, from an analysis of the magnitude and shape of the transitions, it is possible to conclude that this optimum concentration is less than maximum. Since we were never able to produce material which was 100% intercalated in particle sizes which supported superconductivity, there must exist rather sharp concentration gradients at the interface of the intercalated and pure phases. We feel that it is mainly a result of these gradients and inhomogeneous intercalations that a broad (incomplete) transition is seen. The fact that the intercalations are carried out at low temperatures (–40°C) to avoid the formation of the amide means that the reaction rate will be low, and the chance of forming inhomogeneous nonequilibrium intercalation phases is enhanced. As one may expect from a model such as this, the magnitude of the transition was dependent on the degree of intercalation, as determined by the X-ray line intensities. Unfortunately, we were unable to make an intercalated phase sufficiently dilute in strontium so that a decrease in the onset temperature could be seen—mainly due to the fact that at such low concentrations ($\ll 1\%$), the amount of the intercalated phase and, hence, the size of the transition is too small to be seen.

By decreasing the particle size of the starting MoS_2 and by controlling the reactions during the synthesis, we were able to make fully intercalated samples. From electron microscope examinations, the particle size of these samples was found to be in the range less than 1–10 μm. Surprisingly, rather than showing sharper transitions, these samples showed no transition at all, as measured by the ac susceptibility method. This particle-size effect was also observed in fine-particle TaS_2 intercalated with pure ammonia, with strontium plus ammonia, and in fine-particle pure NbS_2, all of which showed superconductivity in large particle size. These fine-particle dichalcogenides were obtained either by reacting finely divided elements for prolonged periods of time at lower temperatures (~400–500°C) or by the reaction of anhydrous metal chlorides with H_2S gas in the range 500–600°C, thus presumably eliminating the defects and dislocations introduced by mechanical grinding.[2]

Even though the powdering effect can be treated as a separate aspect in the observation of

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[2] Thus, it appears that reducing the particle size by mechanical grinding also destroys the superconductivity in the layered dichalcogenides: a well-crystalline ammonia intercalated TaS_2 (which exhibited a well-defined superconducting transition at 4.2°K) was made into fine particles by thorough grinding, after which there was no evidence of superconductivity in spite of the fact that X-ray data indicated the sample was still intercalated. This shows that crystal defects and disorder also play a role.

bulk superconductivity, it is difficult to explain this particle-size effect in the manner which the more conventional superconductors have been treated, i.e., Hg, Ag, etc. (*13*, *14*), mainly because, in our case, the particle sizes are much larger and the critical fields higher. We were also able to rule out the magnetic-field effect described by Gamble et al. (*9*) and sample decomposition which, because of the highly reactive nature of the fine particles, may be expected. It is clear that more work is needed on the disappearance of superconductivity in fine-particle layer compounds.

We have carried out preliminary studies on the other Group VI dichalcogenides intercalated with Sr to see whether superconductivity is induced in these materials as well. The data presented in Table I show that indeed it is. All materials become superconducting below 5.7°K, and as in the case of MoS_2, ammonia is also intercalated along with Sr, and δ is around 3 Å. For comparison purposes, we have examined the intercalation of Sr into 2*s*–TaS_2 by the liquid ammonia method to see whether Sr is solvated by NH_3 in TaS_2 as well. As can be seen from Table I, this is indeed the case, and unlike the case with the Group VI materials, 100% intercalation is achieved, as is the case with pure NH_3 (*9*). $Sr_x(NH_3)_yTaS_2$ material exhibits a sharp and well-defined superconducting transition but with T_{onset} lower (2.8°K) than that obtained with NH_3–TaS_2 compound (4.2°K) (*9*).

Some conclusions of a speculative nature can be drawn from these observations. The fact that superconductivity can be induced in all the Group VI dichalcogenides by alkaline earth metal intercalation indicates that the basic mechanism proposed for alkali metal MoS_2 intercalates appears to hold. However, the covalency of the chalcogen atom, the *d*-band widths involved, and the electron–phonon interactions also seem to play a significant role in determining the T_c. Sr intercalation produces the same T_c in both MoS_2 and $MoSe_2$, but there is a 1.5° decrease in T_c in Sr–WS_2 compared to Sr–MoS_2. Since the empty *d*-band is likely broader in WS_2 than in MoS_2 (*15*), it is possible that the density of states at the Fermi level in intercalated WS_2 is smaller than in intercalated MoS_2. Further, the favorable electron–phonon interaction that raises the T_c from 0.8 to 4.2°K in NH_3–TaS_2 is perhaps offset by a large change in the density of states of the partially filled *d*-band produced by Sr intercalation.[3] It appears that electron-phonon interaction governs the T_c to a greater extent in TaS_2 superconductors than in the Group VI intercalated materials.

The intercalated species discussed above have a diamagnetic core, but the situation changes drastically when we intercalate a paramagnetic species like Eu^{2+}. In a separate publication (*17*), we have reported the properties of Eu intercalated MoS_2 materials and have shown that Eu intercalates along with NH_3 into MoS_2 in compounds prepared by the liquid ammonia method and that the *c* axis expansion is the same as that of $Sr(NH_3)MoS_2$ materials. At low concentrations of Eu, the samples are paramagnetic and exhibit Curie–Weiss law behavior and no superconductivity down to 1.3°K. At high Eu concentrations, the Eu spins order ferromagnetically below 5°K. Thus, the paramagnetic species reduce T_{onset} to immeasurably low values in spite of the fact that electron donation by Eu partially fills the empty *d*-band in MoS_2.

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[3] X-ray photoelectron measurements on pyridine intercalated samples of TaS_2 (*16*) showed a decrease in the electron density on N atoms, indicating a charge donation to TaS_2 layers. Similar results can be expected from NH_3–TaS_2 samples; however, we feel that charge donation from Sr will be greater than that of pure NH_3 because of the fact that pure NH_3 cannot be intercalated into MoS_2 whereas Sr–NH_3 solution can successfully do so and induce superconductivity. Resistivity and Knight shift experiments on Sr samples may prove this point.

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