

## Onset of Superconductivity in Sodium and Potassium Intercalated Molybdenum Disulphide

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Molybdenum disulfide in the form of natural crystals or powder has been intercalated at  $-65$  to  $-70^{\circ}\text{C}$  with sodium and potassium using the liquid ammonia technique. All intercalated samples were found to show a superconducting transition. A plot of the percent of diamagnetic throw versus temperature indicates the possible existence of two phases in the potassium intercalated molybdenum disulfide. The onset of superconductivity in potassium and sodium intercalated molybdenite powder was found to be  $\cong 6.2$  and  $\cong 4.5$  K, respectively. The observed superconductivity is believed to be due to an increase in electron density as a result of intercalation.

There is considerable interest at present in one- and two-dimensional superconducting systems (References 1, 2, and 3). In an attempt to investigate superconductors which are two dimensional in nature, we have introduced metallic sodium and potassium into the layered structure of molybdenum disulphide ( $\text{MoS}_2$ ). In the present communication we report preliminary data which indicate that  $\text{MoS}_2$  intercalated with sodium or potassium is superconducting.

$\text{MoS}_2$  has been extensively studied (Reference 4) and its electrical, magnetic, optical, and structural properties are well known. It has a layered structure, characterized by a high degree of anisotropy as shown in Figure 1. Within each layer there exists trigonal prismatic coordination between the Mo and S atoms, and the bonding in the layer is primarily covalent. Variations in the stacking sequence of the layers result in the formation of two polytypes (Reference 5). These are the 2H (H denoting the hexagonal unit cell) and the 3R (rhombohedral) polytypes. The layers are held together by weak Van der Waals forces. The result of this weak binding is that the interlayer gap may easily be increased to accept alkali metal atoms or ions from an alkali metal-ammonia solution. Chemical and X-ray data for the alkali metal intercalates of  $\text{MoS}_2$  have been obtained by Rudorff (Reference 6). The optical spectrum of  $\text{MoS}_2$  contains two excitonic absorption bands,

of hydrogenic nature (Reference 7), which results from transitions from a spin orbit split valence band (Reference 4).  $\text{MoS}_2$  is not superconducting down to 1.28 K (Reference 8).

The  $\text{MoS}_2$  samples used in the present investigation were crystals of high purity grown by chemical vapor transport,<sup>1</sup> crystals cleaved from a large natural crystal of molybdenite,<sup>2</sup> and purified natural ore.<sup>3</sup> X-ray powder diffraction data indicated that all types of samples were of the 2H polytype. An emission spectrographic analysis of the impurities is shown in Table 1. The  $\text{MoS}_2$  samples were tested for superconductivity prior to intercalation using a self-inductance technique (Reference 9), and none of the samples were found to be superconducting. The samples were intercalated by placing them in a blue sodium-ammonia or potassium-ammonia solution (concentration  $\sim 0.1$  mole percent metal) for  $\sim 72$  h. This was followed by rinsing with liquid ammonia until all traces of excess metal had been removed from the surface, and, finally, by outgassing for 24 h to remove traces of ammonia. All operations were carried out in a high-vacuum system in absence of air.

<sup>1</sup> The authors are indebted to Dr. Fred Gamble of Synvar Associates, Palo Alto, Calif., for supplying the synthetic crystals.

<sup>2</sup> Molybdenite samples obtained from Ward's Natural Science Establishment, Rochester, N.Y.

<sup>3</sup> From Climax Molybdenum Co., Ann Arbor, Mich.

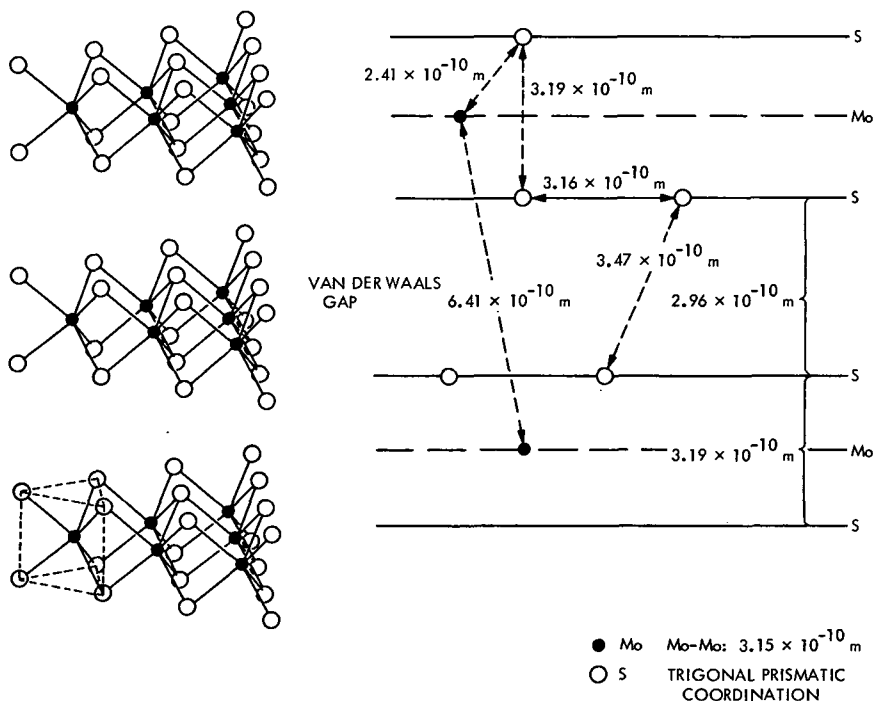


Figure 1. The structure of  $\text{MoS}_2$

The determination of sodium or potassium by means of atomic absorption and chemical analysis showed that the crystals were only partially intercalated and their composition could be represented by  $M_x\text{MoS}_2$  ( $0.1 < x < 0.5$ ), where  $M$  is sodium or potassium. Therefore, the amount of metal was less than in the specimens prepared by Rudorff (Reference 6), and this result could be attributed to insufficient intercalation time. The fact that the intercalations were not complete was confirmed by X-ray analysis of the sodium or potassium intercalates carried out in absence of air. The X-ray results indicated the presence of both unintercalated as well as intercalated  $\text{MoS}_2$ .

In addition, the  $C_0$  dimension of sodium and potassium intercalated samples expanded by  $1.5 \times 10^{-10}$  and  $4.07 \times 10^{-10}$  m (1.5 and 4.07 Å), respectively. The expansion of the  $C_0$  dimension of the sodium intercalated molybdenite crystal is approximately half that found by Rudorff. This is probably due to the sodium ions occupying the octahedral holes in only one of the two Van der Waals gaps in the unit cell, and would imply a stage two-type intercalation.

Table 1. Emission spectrophotographic analysis of impurities in  $\text{MoS}_2$

Component	Molybdenite (natural crystals), <sup>a</sup> ppm	Synthetic crystals, <sup>b</sup> ppm	Molybdenite purified natural ore, <sup>c</sup> ppm
Si	1200	<100 (not detected)	
Fe	870	230	590
Cu		17	
Ca	550	<10 (not detected)	
Mg	10	6.5	
C	900		2000
$\text{MoO}_3$			140
Oil			240
$\text{H}_2\text{O}$			350
Acid insoluble			220

<sup>a</sup> Purity = 99.6%.

<sup>b</sup> Purity = 99.97%.

<sup>c</sup> Purity = 99.65%.

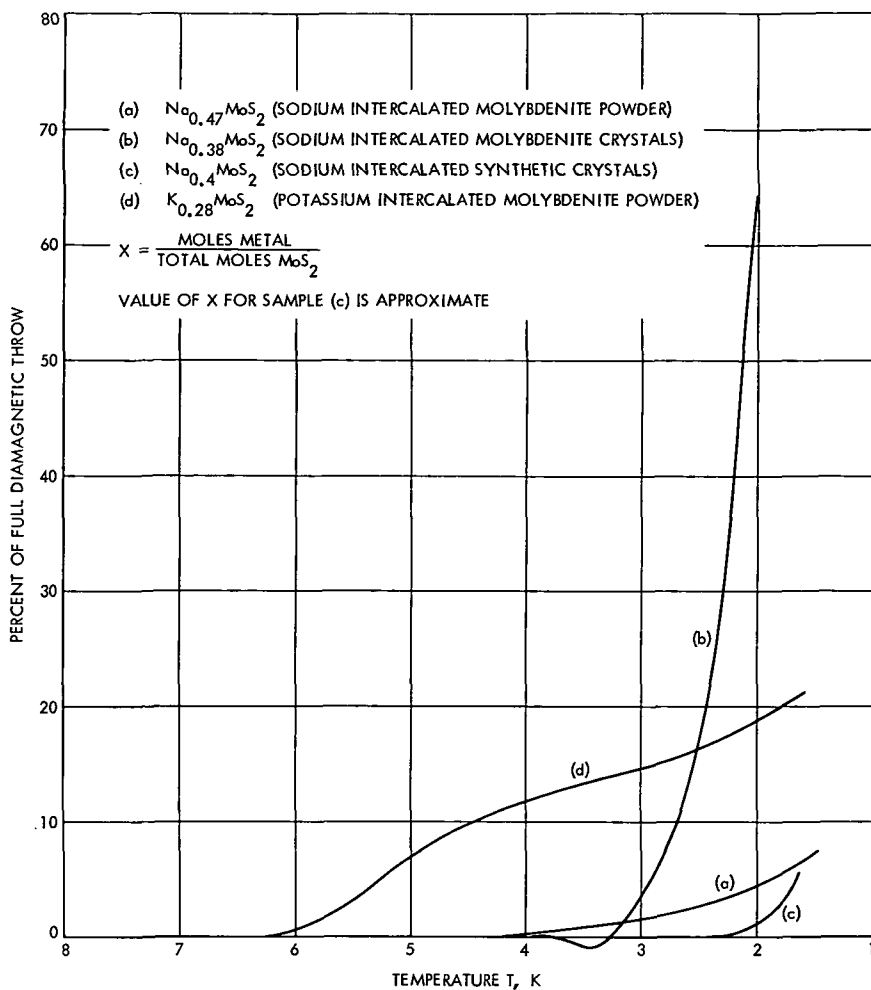


Figure 2. Onset of the superconducting transition in intercalated samples

All intercalated samples exhibited a superconducting transition (Figure 2). In Figure 2, the percent of the full diamagnetic throw is plotted against absolute temperature for potassium and sodium intercalated samples. The percent of the full diamagnetic throw observed in the samples studied was determined by calibration runs using several volumes of either lead or niobium. The sodium intercalated molybdenite powder (curve a) exhibits a wider transition than that observed for sodium intercalated molybdenite crystals (curve b). A sharper transition is found as expected in pure synthetic crystals (curve c). The onset of superconductivity in the potassium intercalated molybdenite powder (curve d) is approximately 2.3 deg higher than the sodium intercalated powder (curve a). At the present stage of investigations, the differences in the onset of the superconducting transitions shown by different alkali metals are not well understood. The shape of curve d indicates the possible existence of a second phase in the potassium

intercalated molybdenite powder. This could be due to two different coordinations of the potassium atoms in the Van der Waals gap or to two different stages of intercalation. Preliminary X-ray powder diffraction data seem to corroborate the existence of two phases (the 002 line is unusually broad). It is hoped that X-ray examination of intercalated single crystals might yield a definite answer to this question.

Superconductivity in these intercalates of  $\text{MoS}_2$  is believed to be due to electrons from the alkali metal going into the unfilled d-band of  $\text{MoS}_2$ . The increase in free electron charge density increases the transition temperature of  $\text{MoS}_2$  to the measurable values found in this investigation. This process utilizes the proposed band structure (Reference 10) and has been suggested previously in the interpretation of optical data on  $\text{Na}_x\text{MoS}_2$  (Reference 11). Work is presently underway to determine the mechanism of the observed superconductivity, the effects of different alkali metals, and the effect of crystal orientation on the superconducting transition.

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