Superconductivity in Intercalated Molybdenum Disulfide*

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Molybdenum disulfide has been intercalated with sodium and potassium. Both natural crystals of molybdenite and synthetic crystals were used, and measurements made on the intercalated products indicate a superconducting transition temperature of ~1.3°K for sodium and ~4.5°K for potassium.

There is considerable interest at present in one- and two-dimensional superconducting systems.[1-3] 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 disulfide (MoS_2). In the present communication we report preliminary data which indicate that MoS_2 intercalated with sodium or potassium is superconducting.

MoS_2 has been extensively studied[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 Fig. 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.[5] These are the 2*H* (*H* denoting the hexagonal unit cell) and the 3*R* (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 MoS_2 have been obtained by Rudorff.[6]

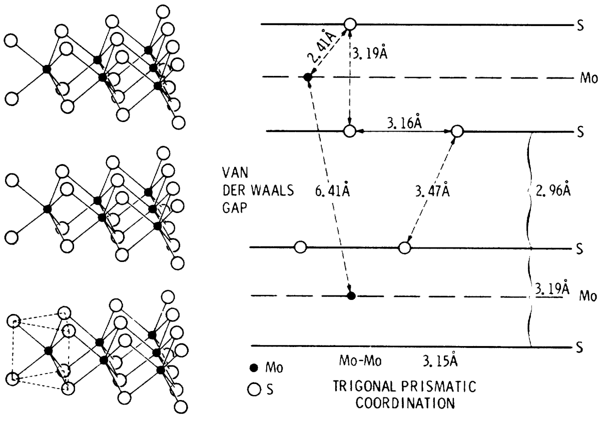

FIG. 1. The structure of MoS_2.

The optical spectrum of MoS_2 contains two excitonic absorption bands, of hydrogenic nature,[7] which results from transitions from a spin-orbit-split valence band.[4] MoS_2 is not superconducting down to 1.28°K.[8]

The MoS_2 samples used in the present investigation were crystals of high purity grown by chemical vapor transport,[9] crystals cleaved from a large natural crystal of molbydenite,[10] and purified natural ore.[11] X-ray powder diffraction data indicated that all types of samples were of the 2*H* polytype. An emission spectrographic analysis of the impurities is shown in Table I. The MoS_2 samples were tested for superconductivity prior to intercalation using a self-inductance technique,[12] 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 ~0.1 mole% metal) for ~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.

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_xMoS_2 ($0.1 \leq x \leq 0.5$), where M is Na or K. Therefore, the amount of metal was less than in the specimens prepared by Rudorff,[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 MoS_2.

In addition, the C_0 dimension of sodium- and potassium-intercalated samples expanded by 2.8 and 4.0 Å, respectively.

All intercalated samples exhibited a supercon-

TABLE I. Emission spectographic analysis of impurities in MoS_2 (ppm).

	Molybdenite (natural crystals)	Synthetic crystals	Molybdenite purified natural ore	
Si	1200 1200	< 100 (not detected)	MoO_3	140
Fe	870	230	Fe	590
Cu	• • •	17	Oil	240
Ca	550	< 10 (not detected)	H_2O	350
Mg	10	6.5	C	2000
C	900	• • •	Acid insoluble	220
Purity	~99.6%	99.97%	Purity	99.65%

ducting transition (Fig. 2). For the sodium-intercalated samples, the transition was not complete down to 1.4°K (our low-temperature limit). The onsets of the transitions were observed at 3 to 4°K and the transitions were quite wide (~ 2°K at the 1.4°K limit) as one would expect from impure, anisotropic specimens. The purer synthetic crystals intercalated with sodium exhibited a much sharper (~1- to 1.5°K-wide) transition which started at ~ 2.0°K. A value of T_c ~ 1.3°K could be estimated from this transition. The potassium-intercalated purified natural ore yielded a more complete transition (~ 4°K wide) with T_c ~ 4.5°K.

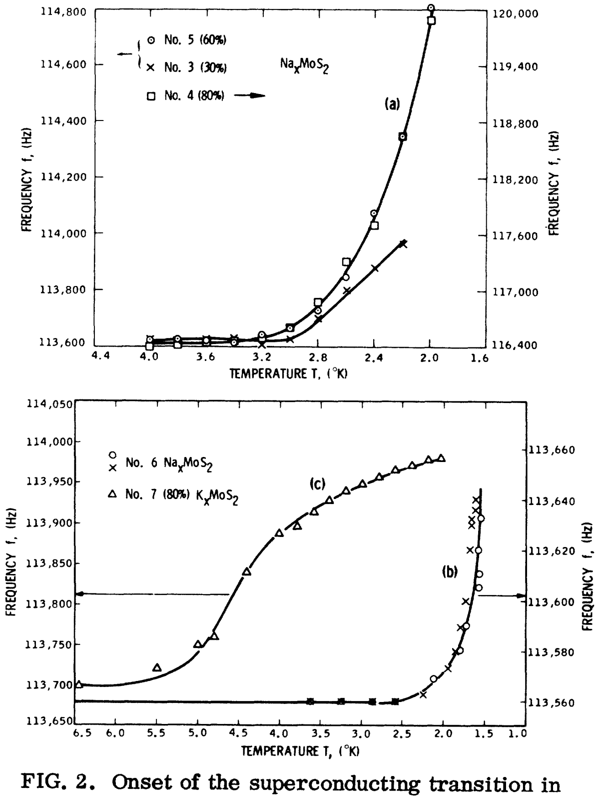

FIG. 2. Onset of the superconducting transition in (a) intercalated natural crystals of molybdenite, (b) intercalated synthetic crystals of MoS_2, and (c) intercalated purified natural ore. The percentage of the sample intercalated is shown in parentheses. (Preliminary chemical analysis of sample No. 6 indicates that it is 65% intercalated.)

In order to estimate the percent of intercalated volume which is superconducting at the low-temperature limit in the samples studied (see Fig. 2), calibration runs were carried out using several volumes of either lead or niobium. From the calibration curves the following percentages of superconducting intercalated volumes were obtained: Sample No. 3, 55%; sample No. 5, 65%; sample No. 6, 10%; and sample No. 7, 10%.

Superconductivity in these intercalates of MoS_2 is believed to be caused by electrons from the metal going into the unfilled *d* band of MoS_2. The increase in free-electron charge density increases the transition temperature of MoS_2 to the measurable values found in this investigation. This process utilizes the proposed band structure[13] and has been suggested previously in the interpretation of optical data on Na_xMoS_2.[14] 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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Theory of the Electronically Induced Crystallographic Transition

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An exactly solvable model is formulated for the electronically induced crystallographic transition. The model contains the essential and new feature that the distortion is conceived to be an operator. This entails a better understanding of the processes involved in this type of transition.

One of the possible explanations of the metal-nonmetal transition is in terms of the electronically induced crystallographic transition. This transition is thought to be a product of the competition between the lattice energy and the energy of the electrons. A crystalline distortion will split up the energy bands resulting in a lower energy of the electron system in case the original conduction band is partly filled, while the lattice energy is raised by the distortion. In this way a competition between the lattice and electronic energies is obtained.

This effect has been studied by Adler and Brooks.[1] Starting from a linear chain of δ potentials they obtained criteria for this type of transition. These criteria were applied to several models, e.g., a model in which the energy bands are spherical around the conduction- and valence-band edges. In most cases Adler and Brooks obtained a first-order phase transition. The case of a linear chain of one-dimensional δ potentials, however, always gives rise to a second-order phase transition as has been shown recently.[2] The effect was also studied by Labbé and Friedel.[3,4] Their three-dimensional model exhibits a first-order phase transition.

The theory of the electronically induced crystallographic transition as formulated up till now is a static theory; i.e., the electron-lattice interaction introduced by the distortion is described by a parameter. Minimization of the total free energy with respect to this distortion parameter yields the equilibrium value of the distorted system for a fixed temperature and also determines the order of the phase transition.

The purpose of this paper is to present a dynamic theory of the electronically induced crystallographic transition; i.e., the distortion is considered to be an operator.[5] The great advantage of this dynamic model with regard to the static model is that the equilibrium value of the distortion can be calculated directly by means of the methods of quantum statistical mechanics without resorting to the minimization procedure. This is significant because the real nature of the electron-lattice interaction, which is intro-