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Heat Capacity of Superconducting Ternary Molybdenum Sulfides

Abstract. *The heat capacities of $AgMo_4S_5$, $PbMo_6S_7$, and $SnMo_5S_6$ are reported. These ternary molybdenum sulfides have been found to be bulk superconductors with very large values of electronic heat capacity coefficients and very low values of Debye temperatures.*

Recently a number of new ternary sulfides have been synthesized (*1*), some of which were found to be superconducting, with reasonably high transition temperatures (*2*). We report here preliminary heat capacities of a few of these molybdenum sulfides. The results are interesting in that for these compounds the electronic heat capacity coefficients, γ, are very high, whereas the Debye temperatures, θ_D, are very low. These sulfides have also been found to be bulk superconductors.

The compounds were prepared by reacting appropriate quantities of the high-purity elements at ~ 1150°C for a day or so. Samples for heat capacity measurements weighing 3 to 5 mg each were prepared by pressing the powders into thin disks and resintering them at 1150°C for a day. Measurements were made by the a-c heat capacity technique (*3*) between 4.2° and 20°K.

Results for the silver, lead, and tin molybdenum sulfides are given in Table 1. For comparison, literature values for a few elements, a few compounds with the β-tungsten structure, and two layered compounds based on TaS_2 are also given. The γ and θ_D values were deduced from the plots of heat capacity C divided by the absolute temperature T versus T^2, which were found to be linear up to ~ 15°K; beyond ~ 15°K θ_D seemed to increase by a few percent.

The $\Delta C/\gamma T_c$ value for $AgMo_4S_5$, which showed a sharp anomaly at the critical temperature T_c, is very close to the Bardeen-Cooper-Schrieffer value of 1.43. The quantity $\Delta C/\gamma T_c$ was not evaluated for the lead and tin compounds, which showed broad superconducting transitions as a result of sample inhomogeneity. The values of γ for these ternary molybdenum sulfides are comparable to or even higher than those of some of the β-tungsten compounds with high T_c values, whereas their Debye temperatures are very much

Table 1. Heat capacities.

Element or compound	γ		θ_D (°K)		$\frac{\Delta C}{\gamma T_c}$	T_c (°K)		Reference
	mj °K^{-2} g-mole^{-1}	mj °K^{-2} g-atom^{-1}	θ calculated from specific heat per gram-mole	θ calculated from specific heat per gram-atom		T_c onset from specific heat data	T_c from magnetic data	
Mo	1.8	1.8	460	460		0.92		(*4*)
$AgMo_4S_5$	98	9.8	64	139	1.5	11.5*	8.3	
$PbMo_6S_7$	353	25.2	79	190		10.6	11.1	
$SnMo_5S_6$	316	26.4	81	186		10.9	10.9	
Nb	7.8	7.8	277	277		9.17		(*4*)
Nb_3Sn	52	13	164	260	2.4	18.0		(*5*)
Nb_3Al	30	7.5	290	460	2.4	18.6		(*6*)
V	9.9	9.9	399	399		5.37		(*4*)
V_3Si	68	17.0	440	700	1.5	16.9		(*7*)
V_3Ga	97.2	24.3	190	302	1.6	14.8		(*7*)
Ta	6.0	6.0	258	258		4.39		(*4*)
TaS_2	8.5	2.83	174	251	1.43	0.8		(*8*)
TaS_2-(2,6-dimethyl pyridine)$_{1/5}$	9.5		106		0.65	2.8		(*8*)
TaS_2-(pyridine)$_{1/2}$	8.9		98		0.80	3.7		(*8*)

* The high value for the $AgMo_4S_5$ sample is caused by contamination during the copper-plating procedure used in mounting samples for specific heat measurements.

lower. In comparison to layered superconductors based on TaS_2, the ternary molybdenum sulfides have higher γ, lower θ_D, and much higher T_c values.

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Electron Diffraction of Wet Proteins: Catalase

Abstract. *Electron diffraction patterns having 3500 reflections out to 2 angstroms were obtained from wet microcrystals of catalase. No diffraction was obtained if the water vapor pressure was set below 90 percent of the equilibrium value.*

Since vacuum drying usually disorders biological materials, electron diffraction with high-vacuum electron microscopes has been applied to a very limited extent in biological structure analysis. This is particularly unfortunate in cases where large crystals suitable for x-ray diffraction cannot be grown, but microcrystals of a suitable thickness for electron diffraction are available. Also, many biological structures, such as cell membranes, occur only in single layers and rarely in stacked arrays. Electron diffraction data in these cases could be of considerable aid in determining the structures. We have developed equipment that can modify any electron microscope to allow microscopy and diffraction of wet specimens. The detailed electron diffraction patterns of catalase we have obtained not only show that the hydration chamber is fully efficient, but also suggest that electron diffraction of wet biological materials is capable of giving detailed structural information. In this work we have also taken steps to minimize radiation damage.

Many attempts have already been made at constructing hydration stages for electron microscopes, some of them with considerable success [for examples, see (*1*)]. Most of these stages involved the use of thin-film windows, which allowed penetration of the electron beam but acted as barriers to the gas. The disadvantages of the thin-film approach are the fragility of the windows (especially in the presence of water vapor); the long preparation times involved; the scattering of the electron beam by the windows, which raises the background level; and the contamination buildup at the windows, which aggravates the scattering problem. We have built differentially pumped hydration stages for a JEOLCO 200-kev and a Siemens IA microscope which, to a large degree, overcome the disadvantages listed above (Fig. 1). The stage consists of four collinear apertures through which the electron beam penetrates, the specimen being positioned between the inner two 75-μm apertures. A pressure gradient is maintained across the apertures by having a source of water vapor feeding the specimen and differentially pumping on the low-pressure side of the apertures. The pressure around the specimen, which was monitored by a mercury manometer, was controlled by varying the temperature of the source. The normal working temperature was 25° to 27°C, so that the measured pressure at the specimen position was 25 to 27 torr. The detailed results of testing the equipment with respect to hydration efficiency, the microscopy of water drops, and the resolution in relation to total gas pressure will be reported elsewhere.

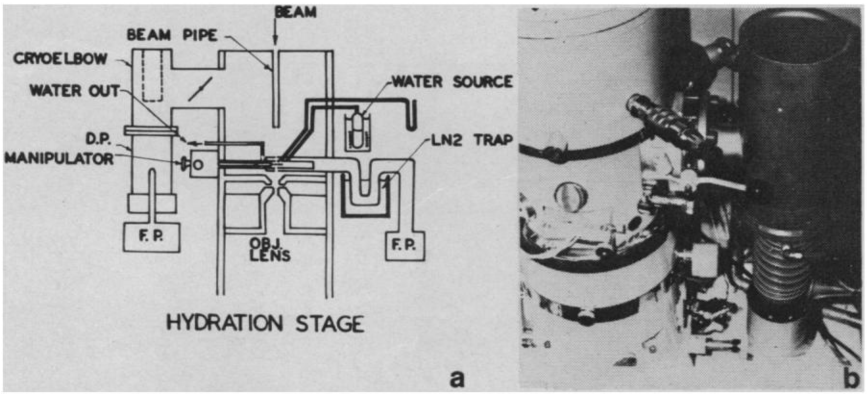

Fig. 1. (a) Schematic of the hydration stage for the JEOLCO 200-kev electron microscope; *D.P.*, diffusion pump; *LN2*, liquid nitrogen; F.P., forepump; *Obj. lens*, objective lens. (b) External appearance of the modified JEOLCO 200-kev with hydration stage.

X-ray diffraction work on catalase (*2*) indicated that diffraction was lost at relative humidities below 93 percent, so that the electron diffraction patterns should indicate the hydration efficiency of our chamber. We evaluated a number of recrystallization techniques for Boehringer and Mannheim ox-liver catalase for perfection in the resulting platelike habit of the microcrystals. The microcrystals were first negatively stained with phosphotungstate (2 percent, *p*H 5.5) (*3*, *4*), and the electron diffraction patterns of the dried crystals were taken. The maximum number of diffraction orders obtained from these crystals was used as the criterion for judging the crystallization procedure that gave the most ordered crystals. We chose a procedure of recrystallization from phosphate similar to that described by Sumner and Dounce (*5*), which gave a large number of plate crystals and a small number of prism