

# Investigation of the heat capacity and of the superconducting properties of the sulfide $\text{Mo}_6\text{NaS}_8$

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The heat capacity and the temperature dependence of the critical field of the superconducting molybdenum sulfide  $\text{Mo}_6\text{NaS}_8$  was measured. It is shown that, in contrast to  $\text{Mo}_5\text{SnS}_6$ , the value of  $C_p/T$  above the critical temperature deviates little from a linear function of  $T^2$ . We determined the Debye temperature  $\theta_D = 118$  K, the Sommerfeld constant  $\gamma = 9.2 \times 10^{-3} \text{ J/K}^2 \text{ mole}$ , the derivative  $(dH_{c2}/dT)_{T=T_c} = 12.8 \text{ kOe/K}$  and the critical field  $H_{c2}(0) = 100 \text{ kOe}$ .

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We have already reported<sup>[1]</sup> that some molybdenum sulfides doped with alkali metals are superconducting, one of them being  $\text{Mo}_6\text{NaS}_8$ . The transition temperature of this compound is approximately 8.6 K. On the other hand, mention was made in some earlier papers that no superconductivity has been observed in the Mo-Na-S system.<sup>[2]</sup> It was of interest to carry out a detailed investigation of the system  $\text{Mo}_6\text{Na}_x\text{S}_8$ , and to study, in particular, its heat capacity.

We used for the measurements samples prepared, as before,<sup>[3]</sup> by synthesis of molybdenum, sulfur, and  $\text{Na}_2\text{S}$ , the contents of which were determined by the stoichiometric composition of the compound. Powders of the aforementioned components were pressed into cylinders of 9 mm diameter. The synthesis was carried out in quartz ampules filled with helium at 900 °C, after which the powder of the obtained compound was compressed to make up the samples. To investigate the superconducting properties and the heat capacity we usually employed cylinders of 5 and 9 mm diameter, respectively. The mass of the

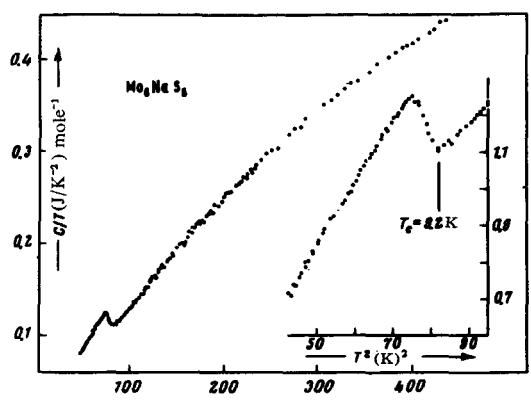


FIG. 1. Plot of  $C_p/T$  against  $T^2$  for  $\text{Mo}_6\text{NaS}_8$ .

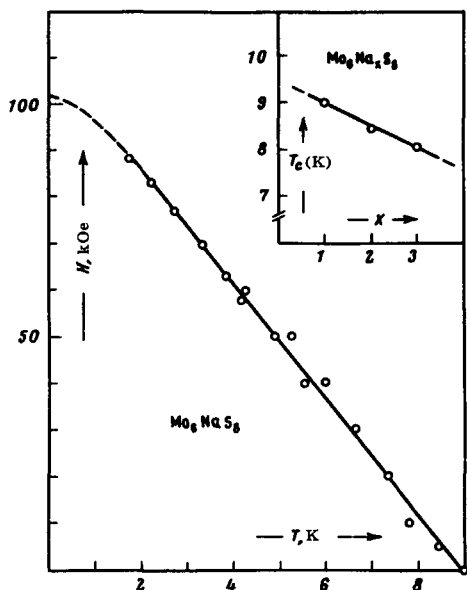


FIG. 2. Plots of the temperature dependence of the critical field of  $\text{Mo}_6\text{NaS}_8$ . In the upper right corner is shown the dependence of the critical temperature of  $\text{Mo}_6\text{Na}_x\text{S}_8$  on the sodium content.

sample used to measure the heat capacity was approximately 8 g, i.e.,  $9.5 \times 10^{-3}$  g mole. (It should be noted that when samples of molybdenum sulfides with alkali metals are stored in air they decompose and do not become superconducting, in contrast to samples stored in a helium atmosphere, whose properties remained constant). The heat capacity was measured in a calorimeter whose construction was described earlier in<sup>[4]</sup>. Figure 1 shows a plot of  $C_p/T = f(T^2)$ , while Fig. 2 shows a plot of  $H_{c2}(T)$  obtained from measurements of the sample resistance.<sup>2)</sup> As seen from these figures, the critical temperature of the  $\text{Mo}_6\text{NaS}_8$  sample is 9 K, and  $(dH_{c2}/dT)_{T=T_c} = 12.8$  kOe/K. In contrast to  $\text{Mo}_5\text{SnS}_6$ ,<sup>[5,6]</sup>  $C_p/T$  of  $\text{Mo}_6\text{NaS}_8$  as a function of  $T^2$  deviates little from linearity at temperatures above critical. From an analysis of this dependence it follows that the Debye temperature is  $\Theta_D = 118$  K, the coefficient  $\gamma C_p$  in the electron contribution to the heat capacity is equal to  $(9.2 \pm 0.5) \times 10^{-3}$  J/K<sup>2</sup> mole, and  $(\Delta C_p/\gamma T)_{T=T_c} = 3.03$ . If we use  $(\Delta C_p/\gamma T)_{T=T_c}$ , the value  $(dH_{c2}/dT)_{T=T_c}$ , and the residual resistivity,  $3.2 \times 10^{-4}$   $\Omega$  cm for the investigated sample, then we can calculate  $\gamma_H$  (see<sup>[7]</sup>). It turns out here that  $8.2 \pm 0.4 \times 10^{-3}$  J/K<sup>2</sup> mole, i.e., it agrees well with  $\gamma C_p$ .

As noted above,  $C_p/T$  as a function of  $T^2$  is not strictly linear. The slight deviation from linearity can be regarded (just as in the case of  $\text{Mo}_5\text{SnS}_6$ <sup>[5]</sup>) as a consequence of the Einstein contribution to the lattice heat capacity of the investigated system. In this case  $\Theta_E$  should be considerably higher than for  $\text{Mo}_5\text{SnS}_6$ , whereas the coefficient "a" of the Einstein term in the expression for the heat capacity should be small. On the other hand, the above-mentioned small deviation from linearity should result from the fact that the Debye temperature of this system is equal to 118 K, i.e., it is relatively small and therefore the cubic relation for  $C_p(T)$  no longer holds at temperatures exceeding 12 K.

A characteristic feature of  $\text{Mo}_6\text{NaS}_8$  is also the fact that this molybdenum sulfide, having a relatively high superconducting transition temperature  $T_c = 9$  K, is destroyed by a relatively weak magnetic field. As seen from Fig. 2, the values of  $H_{c2}(0)$  and  $(dH_{c2}/dT)_{T=T_c}$  are 100 and 12.8 kOe/K, respectively, which is not more than a third the value for molybdenum sulfides with Pb and Sn.

At the present time it is still difficult to say whether there exists any connection between the quantities  $H_{c2}(0)$ ,  $(dH_{c2}/dT)_{T=T_c}$ , and the singularities of the phonon spectrum. It can be noted, however, that it follows from our results of the measurements of the heat capacity of three-component molybdenum sulfides such as  $\text{M}_x\text{Mo}_6\text{O}_8$  that whenever the metal M has a relatively low mass the lattice part of the heat capacity satisfies the Debye law, while  $H_{c2}(0)$  and  $(dH_{c2}/dT)_{T=T_c}$  have relatively low values.

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<sup>2</sup>The measurements of  $H_{c2}(T)$  were made at the International Laboratory for Strong Magnetic Fields and Low Temperatures in Wrocław (Poland).

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