The heat capacity of molybdenum chalcogenides

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(Submitted 14 April 1982)
Zh. Eksp. Teor. Fiz. **83**, 1500–1514 (October 1982)

Results are given of heat capacity measurements on halogenated chalcogenides at low temperatures. The results are compared with literature values and those published earlier by the present authors. The parameters of the compounds studied, calculated from the results of measuring the heat capacity and superconducting properties, are presented. The possibility of regarding ternary molybdenum chalcogenides as quasi-binary inclusion compounds consisting of Mo_6Ch_8 clusters and atoms of the third component is discussed.

PACS numbers: 65.40. – f

INTRODUCTION

There have recently been intense studies of the thermal properties of a whole range of compounds of transition metals with different metalloids. Many such compounds have not only metallic conductivity (i.e., their resistivity decreases on lowering the temperature) but also turn out to be superconductors.1) Bronzes, carbides, nitrides, some clathrates, chalcogenides, etc., are included among these compounds. The features of the behavior of such compounds are often related to band structure details, but also depend to an appreciable extent on the characteristics of the phonon spectrum.

Binary and multicomponent molybdenum chalcogenides are now being studied intensely and among them many are superconductors. As is well known,[2] the critical temperature of these compounds reaches 15 K, and the critical magnetic fields, for some of them exceed 500 kOe.

Important information necessary for understanding the physical properties in general and features of the superconductivity in particular can be obtained from a study of the heat capacity of such systems. Studies of molybdenum chalcogenides (MCh's) carried out by us have shown[3-9] that the temperature dependence of the heat capacity at low temperatures can be very different for different MCh's (see Fig. 1). The Debye law is obeyed up to 15 K for some MCh's, i.e.,

$$C_L(T)\sim(T/\theta_D)^3; \tag{1}$$

the magnitude of the heat capacity is relatively small. Such chalcogenides include Mo_6Ch_8, $NaMo_6Sh_8$, and $Cu_{1.8}$-Mo_6Ch_8.[7,9] Other MCh's, mainly those which have high superconducting parameters, have a more complicated temperature dependence of heat capacity which then has a relatively high value. Such chalcogenides include $PbMo_6S_8$, $PbMo_6Se_8$, and $SnMo_6S_8$.[3,4,8-10]

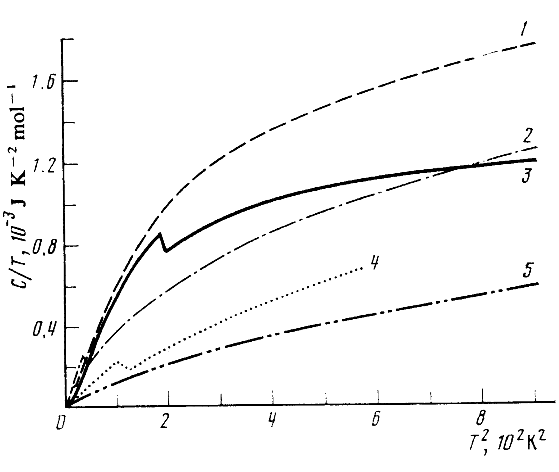

FIG. 1. Dependence of C/T on T^2 for some molybdenum chalcogenides: 1—$PbMo_6Se_8$, 2—Mo_6Se_8, 3—$PbMo_6S_8$, 4—$Cu_{1.8}Mo_6S_8$, 5—Mo_6S_8. The lines are obtained by averaging the experimental specific heat values (the experimental values do not scatter by more than 2%).

Since the heat capacity of the MCh's studied consists of only the lattice, C_L, and electronic, C_E, contributions, the observed difference in the temperature dependence can be ascribed to the complicated structure of the phonon spectrum. For cases where the lattice part can be approximated by the Debye formula, the coefficient γ of the electronic term is determined from a plot of $C_{\exp}/T=f(T^2)$. Such a method is not always applicable for MCh's, since for many of them $C_L(T)$ is a complicated function.

A new method of calculation had, therefore, to be found for analyzing the experimentally determined temperature dependence of heat capacity of MCh's. The problem consisted in finding such physical bases of expressions for $C_L(T)$as would satisfy the following criteria for the values found for their parameters:

1) Agreement between calculated and experimental values of $C_L(T)$ above T_c within the experimental limits of uncertainty (2%).

2) Agreement between calculated and experimental values of entropy in the normal state over the whole temperature range studied to the same accuracy.

3) The absence of a temperature dependence of the difference $C_{\exp}/T-C_LT$; this assumes that the coefficient γ in the electronic heat capacity remains constant.

It was found from the result of numerical comparison of the calculated and experimental values of the heat capacity that the requirements listed were satisfied with the best accuracy by the following expression:

$$C_L=A_1C_1(\theta_1)+A_2C_2(\theta_2)+A_3C_3(\theta_3). \tag{2}$$

Here $C_1(\theta_1)$ is the full Debye function ($\theta_1=\theta_D$), $C_2(\theta_2)$ is the full Debye function for binary MCh's ($\theta_2=\theta_{D2}$) or the Einstein function for ternary MCh's ($\theta_2=\theta_E$), $C_3(\theta_3)=\beta T^3$, where the temperature $\theta_3=\theta_{D3}$ is determined from the adjustable parameter $\beta\pm A_1, A_2$ and A_3 are weighting factors:

for binary compounds $A_1 = A_2 = 1$, $A_3 = 12$; for ternary compounds $A_1 = 1$; $A_2 = 0.4$ to 1, $A_3 = 13$.

The values of A_1 and A_2 were determined in the numerical analysis since it was not known, *a priori*, which of the available degrees of freedom will be thermally excited in the temperature range studied and what form of contribution this can make to the heat capacity. Quantitative agreement within 2 to 10% between calculated and experimental values can be achieved by representing C_L as the sum of only the first two terms, but there are departures, regular in character, which occur for a number of compounds. They appear at temperatures between 15 and 20 K, increasing with increasing temperature, and at $T > 15$ K the experimental values $C_{\exp}$ for such compounds exceed those calculated systematically. This is evidence of the existence of an additional contribution to the heat capacity which is not included in such a representation of C_L. The term $C_3(\theta_3)$ is introduced into the expression for C_L to take this contribution into account, and it can be related to intra-cluster oscillations.

The model considered comes from considering MCh's as inclusion compounds consisting of quasi-rigid Mo_6Ch_8 units with atoms A incorporated in the spaces between them, i.e., compounds consisting of light A atoms and heavy Mo_6Ch_8 clusters. Molybdenum chalcogenides have similar properties to compounds which also consist of two components of very different masses (for example PdH). Mössbauer studies,[3,11,12] inelastic neutron scattering,[13–18] and also theoretical calculations[19,20] enable the phonon spectrum of MCh's to be thought of in the following way. The phonon spectrum of binary systems can be represented by a model in the form of a sum of 6 external modes (consisting of three acoustic translational and three torsional) and 36 hard intra-cluster modes. There are an additional 3 low-frequency optic modes in the phonon spectrum, related to oscillations of atoms A, in the case of ternary systems.[17,18] The optic modes are strongly anharmonic and anisotropic. Atom A then takes part not only in optic modes of oscillation but can also appreciably affect the Mo_6Ch_8 torsional oscillations. More reliable results can be obtained than before[21] by using such a model in treating the experimental results.

Published work devoted to the measurement of the heat capacity of MCh's at low temperatures can be classified as follows. In some of them C_L is represented in the form of a function $\propto T^3$ or by a polynomial, after which the electronic term γ is determined from the experimental $C_{\exp}(T)$. However, since the system is in the superconducting state at low temperatures, the values of C_E and γ obtained in this way are unreliable. On the other hand, the polynomial used, $C_L = A_1T^3 + A_2T^5 + A_iT^{2i+1}$ (just as a similar polynomial for $S(T)$ used to determine C_E) is unsuitable for determining γ, since very different values are obtained depending on the magnitude of the coefficient A_i.

In a number of cases G is evaluated from the jump in heat capacity $\Delta C(T)$, using the BCS model. The value of the electron-phonon interaction constant, λ_{ep}, and the density of states at the Fermi surface, $N(E_F)$, can be determined from the value of γ obtained. Such results together with known values of λ_{ep} and $N(E_F)$ obtained by other methods are collected together in Table I (here ω_D, ω_E and ω_i are the Debye, Einstein and intra-cluster frequencies).

EXPERIMENT

Ternary and some binary molybdenum chalcogenides were prepared by direct synthesis of the element at high temperatures. In a number of cases sulfides of the metals which were the third components were used for synthesis of ternary molybdenum chalcogenides (TMCh's), for example Na_2S.

TABLE I.

	C_L, J K^{-1} mol^{-1}	γ, 10^{-3} J K^{-2} mol^{-1}	λ_{ep}	$N(E_F)$, States (ev·Atom-spin)$^{-1}$
$PbMo_6S_8$	$\theta_D = 79$ K [22] $\omega_D = 70$ K, $\omega_E = 140$ K, $\omega_i = 456$ K [13]	353 [22] 70.8 [23] 105 [14]	2.5 [20] 1.2 [23]	0.33 [20]; 0.53 [25] 0.57 [14] 0.63 [24]; 0.63 [26]
$SnMo_6S_8$	$\theta_D = 81$ K [22] $\omega_D = 74$ K, $\omega_E = 155$ K, $\omega_i = 456$ K [13]	316 [22] 60.7 [23] 79.5 [14]	1.13 [14]	0.55 [26] 0.55 [24] 0.43 [14]; 0.42 [27]
$Cu_2Mo_6S_8$	–	54 [28]	1.06 [28]	0.35 [28] 0.35 [24]; 0.35 [26]
$AgMo_4S_5$	$\theta_D = 64$ K [22]	98 [22]	–	–
$LaMo_6S_8$	$\theta_D = 356$ K [29]	28 [29]	0.83 [28]	0.20 [28]; 0.19 [29] 0.20 [30]
Mo_6Se_8	$\theta_D = 207$ K [29] $\theta_D = 177$ K [21]	21 [29]; 26 [29] 44 [14]; 47.5 [21]	0.8 [29] 0.8 [14]	0.19 [29]; 0.22 [20] 0.29 [14]; 0.19 [25]
$PbMo_6Se_8$	–	28 [14]	0.67 [14]	0.20 [14]; 0.23 [20] 0.37 [24]; 0.15 [25]
$SnMo_6Se_8$	–	–	–	0.38 [27]
$LaMo_6Se_8$	$\theta_D = 205$ K [29]	53 [29]; 76 [29] 79 [28]	1.01 [29] 1.06 [28]	0.53 [29] 0.54 [28]

Synthesis was usually carried out in a quartz ampoule filled with clean inert gas. By subsequent grinding, pressing, and homogenizing annealing, sintered specimens could be obtained with sufficiently good conductivity and narrow width of the superconducting transition.[4]

Specimens of Mo_6S_8 were obtained by many-fold extraction of metal A from TMCh's with the help of dilute hydrochloric acid. The following ternary chalcogenides were used for this purpose: $ZnMo_6S_8$, $NiMo_6S_8$, $Cu_{1.8}$-Mo_6S_8.[9] Halogen substituted MCh's such as $Mo_6Ch_6Y_2$ where $CH = S$, Se and $Y = Br$, I were obtained by the method described earlier.[5] Synthesis of the compound $Mo_6Ch_6Y_2$ was carried out from the elements or from a mechanical mixture of composition $5Mo + 6Ch + MoY_2$.

The temperature, duration of synthesis and homogenization of all MCh's was optimized according to the minimum width of the superconducting transition. Except for halogen substituted MCh's and $LaMo_6S_8$ the size of ΔT_c was not more than 10 to 15% of T_c determined by inductance. It was found that T_c was equal to 1.7 K for Mo_6S_8 specimens, regardless of which original TMCh was used.[32] Determination of the residual content, x, of the third component showed[2] that for Mo_6S_8 obtained from $ZnMo_6S_8$, $x_{Zn} < 10^{-2}$, from $Cu_{1.8}Mo_6S_8$, $x_{Cu} = 2\times10^{-3}$ and from $Ni_2Mo_6S_8$, $x_{Ni} = 7\times10^{-5}$. It can be concluded from these results that the observed superconductivity is not connected with the presence of the remains of the third component. It is more likely that the presence of hydrogen in all specimens leads to stabilization of the system and the appearance of superconductivity.[32]

The specimens studied usually consisted of TMCh's with the Chevrel-phase structure. In a number of cases $MoCh_2$ and $MoCh_3$ were present in them. The content of each of these phases could amount to $\approx 10\%$.[33] The degree of uniformity of the specimens was determined by a microprobe technique. A whole range of different measuring devices was used for experimental studies of MCh's. Heat capacity was measured in a calorimeter with a mechanical heat switch.[10] Measurements were carried out over the temperature range from 2 to 30 K (Ref. 33), and in mangetic fields up to $H = 50$ kOe.[34] Measurements of the magnitude of the critical magnetic field H_{c2} were carried out both in constant (Ref. 35)[3] and in pulsed fields.[36] A standard four-lead method was used to measure the resistivity. The magnetic susceptibility χ was usually measured with a string magnetometer.[37] The critical temperature was measured by an induction method or by the change in resistivity.

The accuracy of the results obtained was not determined by errors in measurements, but depended mainly on the presence of extraneous phases, such as $MoCh_2$ and Mo_2Ch_3, by lattice defects magnetic impurities and from the stoichiometry. The presence of extraneous phases is especially important as they can lead to a reduction in the values of heat capacity measured by up to 15% compared with single-phase specimens.

RESULTS

The temperature dependence of the molar heat capacity of MCh's of composition $A_x Mo_6Ch_8$ is determined to a considerable extent by the third component (see Fig. 1). The entropy S at $T = 20$ K for the MCh's studied can be calculated from the $C(T)$ dependence. These results are shown in Tables II and III. It can be seen from the results given that MCh's with Ag, Cd, Pb and Sn have an appreciably higher entropy than the other MCh's, including those with substituted halogen.

Heavy metals, such as Pb and Sn, with large atomic radii going into the Chevrel-phase lattice and weakly bonded to the Mo_6S_8 clusters, contribute to $C_L(T)$ even at low temperatures. Light atoms (Cu, Zn) on the other hand can be more strongly bonded to Mo_6S_8. Their contribution to the heat capacity will, evidently, only be appreciable at high temperatures.

TABLE II.

	θ_1, K	A_2	θ_2, K	β, 10^{-3} J $K^{-4}\cdot mol^{-1}$	θ_3, K	10^{-3} γ J $K^{-2}\cdot mol^{-1}$	γ_{BCS}, 10^{-3} J$\cdot K^{-2}\cdot mol^{-1}$	$\gamma\Delta$, 10^{-3} J$\cdot K^{-2}\cdot mol^{-1}$	ν_χ, 10^{-3} J$\cdot K^{-2}\cdot mol^{-1}$	χ, 10^{-4} cgs$\cdot mol^{-1}$	ρ, 10^{-4} $\Omega\cdot cm$	d, g$\cdot cm^{-3}$	S(20 K) J$\cdot$K$\cdot mol^{-1}$
$PbMo_6S_8$	108	0.42	48	0 028	411	125	112	110	27.7	3.8	2.0	6 17	10.25
$Sn_{1.2}Mo_6S_8$	124	0.42	41	0.043	356	84	73	74	29 9	4.1	1.9	5.02	9.92
$Cd_{1.2}Mo_6S_8$	104	0.10	39	0.040	365	57	–	–	15.3	2.1	5.7	5.66	9.40
$AgMo_6S_8$	121	0.40	41,5	0.017	485	30	33	24	5.8	0.8	1.5	5.70	8.22
$ZnMo_6S_8$	140	0.38	107	0.015	506	24.5	–	–	21.9	3.0	2.3	5.45	
$Zn_2Mo_6S_8$	136	1	120	0.020	506	25	–	–	–	–	–	–	3.52
$Cu_{1.8}Mo_6S_8$	135	1	103	0.075	482	45	46	40	18.2	2.5	1.8	5.8	4.00
$NaMo_6S_8$	145	1	300	0.030	402	10.9	10.5	8.7	–	–	3.2	5.1	2.95
$LiMo_6S_8$	140	–	–	–	–	13.5	–	–	–	–	3.0	4.8	2.00
Mo_6S_8	140	1	290	0.012	545	28	–	–	22.6	3.1	40	5.2	2.94
$Mo_6S_6Br_2$	138	1	167	0.012	545	71.5	68	64	–		–	5.5	4 67
$Mo_6S_6J_2$	128	1	176	0.028	411	64	71	59	–		–	5.8	5 4
$LaMo_6S_8$	131	1	128	0.004	770	22.6	18	15.4	9.8	1.35	2.0	5.84	3.05

TABLE III.

	θ_1, K	A_2	θ_2, K	β, 10^{-3} J K^{-4}·mol^{-1}	θ_3, K	γ, 10^{-3} J·K^{-2}·mol^{-1}	γ_{BCS} 10^{-3} J·K^{-2}·mol^{-1}	$\gamma\Delta$, 10^{-3} J·K^{-2}·mol^{-1}	γ_χ, 10^{-3} J·K^{-2}·mol^{-1}	χ, 10^{-4} cgs·mol^{-1}	ρ 10^{-4} Ω·cm	d, g·cm^{-3}	S(20K) J.K.mol^{-1}
$PbMo_6Se_8$	85	0.46	51	0.076	294	31	29	26	19	2.6	1.8	7.44	12.5
$SnMo_6Se_8$	102	0.35	48	0.071	301	24	—	—	—	–	—	–	9.85
$CdMo_6Se_8$	87	0.20	23	0.052	334	55	—	—	—	–	—	–	12.9
$ZnMo_6Se_8$	98	1	123	0.044	354	27	—	—	—	–	—	–	6.6
$CuMo_6Se_8$	98	1	125	0.051	336	40	—	—	—	–	—	–	7.0
Mo_6Se_8	95	1	202	0.042	359	75	65	61	34	4.7	—	6.8	8.0
$Mo_6Se_6Br_2$	88	1	228	0.046	350	81	74	73	—	–	—	–	8.87
$Mo_6Se_6J_2$	93	1	182	0.055	329	75	—	—	—	–	—	–	9.0
Mo_6Te_8	85	1	180	0.087	282	20	—	—	—	–	—	–	
$LaMo_6Se_8$	117	1	91	0.018	476	83	84	—	46	6.2	2.1	7.4	6.6

New results of measuring the heat capacity of MCh's in the temperature range $2 \leqslant T \leqslant 30$ K are presented here. These results together with those published by us earlier[2-9] are analyzed with the help of the model presented above. The characteristic parameters of the phonon spectrum are obtained as a result of such an analysis together with values of the electronic heat capacity coefficient γ, which $N(E_F)$, λ_{ep}, the energy gap Δ (0), and the thermodynamic critical field $H_c(0)$ can be found.

The $C_L(T)$ relation for $T < T_c$ was determined from the relation $\gamma T = C_{exp}(T) - C_L(T)$. For compounds with relatively low values of dH_{c2}/dT and T_c, measurements of heat capacity were made in a magnetic field $H \leqslant 50$ kOe. The value of $dH_{c2}/dT)_{T_c}$ obtained from measurements of heat capacity are shown in Table IV. For MCh's with large dH_{c2}/dT and T_c, use was made of the suppression of superconductivity by small amounts of iron impurity.[3-9]

The characteristic parameters for $C_L(T)$ shown in Tables II and III could be calculated according to our proposed model and values of γ determined for all the compounds studied.

The jump in heat capacity at $T = T_c$ was also used to determine γ from the relation for γ_{BCS} which comes from the BCS theory: $\Delta C(T)/T_c = 1.43\gamma$.

TABKE IV.

	$T_c(H=0)$,K	$T_c(H=50$ kOe),K	$(dH_{c2}/dT)_{T_c}$ kOe·K^{-1}
$SnMo_6S_8$	11.7	10.5	42
$AgMo_6S_8$	7.7	2	–
$Cu_{1.8}Mo_6S_8$	10.7	7.5	16
$NaMo_6S_8$	8.7	5.7	17
$LaMo_6S_8$	6.8	3.4	15
$SnMo_6Se_8$	3.4	1.9 (2.6) *	27
$CuMo_6Se_8$	5.9	4.2	29
$LaMo_6Se_8$	11.6	10.9	72
$Mo_6S_6Br_2$	13.0	11.9	45
$Mo_6S_6J_2$	13.1	11.5	35
Mo_6Se_8	6.3	4.3	25
$Mo_6Se_6Br_2$	6.9	5.8	55
$Mo_6Se_6J_2$	4.8	4.0	65

*T_c measured in a field of 20 kOe

In Tables II and III we show values of γ_{BCS}, γ_Δ the coefficient of the electronic heat capacity determined from the jump in heat capacity $\Delta C(T < T_c) = C_{es}(T) - C_{en}(T)$ and also γ_χ determined from the magnetic susceptibility χ. We also show in Tables II and III the results of measuring the electrical resistivity ρ at $T > T_c$ and the density d. The temperature dependence $C_L(T)$ obtained in this way can be compared (see Fig. 2) with the dependence $C_L(T)$ calculated from the known phonon spectra. We cannot expect strict quantitative agreement with the results for $C_L(T)$ because the harmonic approximation was used in calculating $C_{Lp}(T)$. Sufficiently good agreement between $C_L(T)$ and $C_{Lp}(T)$ was obtained, for example, for $PbMo_6S_8$ (Fig. 2) and also for $PbMo_6Se_8$, Mo_6Se_8 and $SnMo_6S_8$. However, there is a large difference between $C_L(T)$ and $C_{Lp}(T)$ for $Cu_{1.8}Mo_6S_8$. The results given earlier[33] for $Cu_xMo_6S_8$ also disagree with the heat capacity calculated from the phonon spectrum. It is possible that this disagreement arises because the phonon spectrum of copper chalcogenides is only known at room

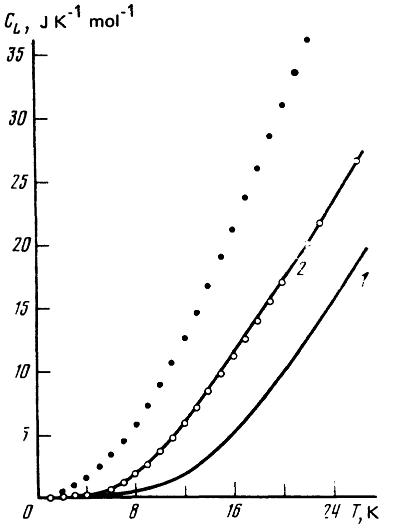

FIG. 2. Comparison of values of $C_L(T)$ calculated from the phonon spectra[17,18] for $Cu_2Mo_6S_8$ (●) and $PbMo_6S_8$ (○), with results obtained for them in the present work (curves 1 and 2 respectively).

TABLE V.

	T_C, K	$\overline{N}(E_F)$, States (eV·atom-spin)$^{-1}$	$\overline{\lambda}_{ep}$	$2\Delta(0)/kT_c$	$H_c(0)$ kOe	$H_{c2}(0)$, kOe	$(dH_{c2}/dT)_{T_c}$ kOe K^{-1}	$H^*_{c2}(0)$ kOe	$dH^*_{c2}/dT)_{T_c}$ kOe K^{-1}	H_{p0} kOe
$PbMo_6S_8$	13.7	0.63	1.85	3.94	3.2	540	58	576	60.6	254
$Sn_{1.2}Mo_6S_8$	11.4	0.49	1.44	4.44	2.3	330	38	302	37.4	215
$Cd_{1.2}Mo_6S_8$	2.4	0.48	0.66	–		58	27	57	34.8	44
$AgMo_6S_8$	7.6	0.31	1.06	3.92	0.8	65	7	63	10.1	140
$ZnMo_6S_8$	2.8	0.21	0.61	2.23	0.2	28	76	30	10.4	51
$Zn_2Mo_6S_8$	3.0	0.20	0.69	3.42	0.2	28	7.6	30	10.4	55
$Cu_{1.8}Mo_6S_8$	10.3	0.30	1.25	3.52	1.3	140	15.5	154	21	189
$NaMo_6S_8$	9.2	0.10	0.07	3.62	0.5	105	12.8	59	9.2	169
$LiMo_6S_8$	4.0	0.11	0.69	–		–	10	28	10.3	74
Mo_6S_8	1.8	0.29	0.46	–		10	7.5	–	–	34
$Mo_6S_6Br_2$	13.3	0.40	1.77	3.60	2.1	340	32	351	38	245
$Mo_6S_6J_2$	13.7	0.36	1.67	3.70	2.1	350	28	305	32	252
$LaMo_6S_8$	7.0	0.18	0.87	3.75	0.6	54	12.5	57	12	129

temperature, while these compounds undergo a phase transition in the region below 300 K.[38]

On comparing our results on the heat capacity of MCh's with those published in the literature[14,25,29,38] and taking the effect of the details of specimen preparation into account, the agreement between them can be regarded as satisfactory (if the discrepancy is not more than 15%). Our results usually lie a few percent higher,[10] which may, in particular, be due to small amounts of impurity. Inexactness in the assumed model for $C_L(T)$ can also be a source of systematic errors. (In view of quantitative estimates of the error, only differences between the mean values of $C_L(T)$ which exceeds 15% can be considered significant).

It can be concluded from the results obtained on the heat capacity of molybdenum chalcogenides that the characteristic temperatures θ shown in Tables II and III are appropriate for describing $C_L(T)$ in the temperature range studied, and also for a sufficiently accurate determination of γ for these chalcogenides. It should be borne in mind that the real lattice dynamics and the corresponding phonon spectra can differ from those of the model, so that the values of θ should only be considered as approximate characteristic temperatures. It should also be remembered that anharmonicity and inhomogeneity of the specimen may affect the vibration spectrum.[12] Since anharmonicity can give a contribution to $C_L(T)$ linear in temperature, a non-electronic contribution to γ_i can be obtained which will, however, not exceed 10% of the values given. Tables V and VI show quantities which have been calculated from the results in Tables II and III, obtained directly from measurements of $C(T)$.

The following symbols are used in these tables: $\overline{\lambda}_{ep}$—the probable value of the electron-phonon interaction constant λ_{ep} (according to all available data); $\overline{N}(E_F)$—the probable value of the density of states at the Fermi surface in units of number of states per eV-spin-atom (according to all available data); $H_c(0)$—the thermodynamic critical field at $T = 0$; $(dH_{c2}/dT)_{T_c}$—the experimental value of the temperature derivative of the upper critical field; H_{c2}—the experimental value of the upper critical field at $T = 0$; (dH^*_{c2}/dT)—the orbital contribution to (dH_{c2}/dT); $H^*_{c2}(0)$—the orbital contribution to $H_{c2}(0)$; H_{p0}—the paramagnetic limit; Δ (0) the energy gap at $T = 0$ K.

TABLE VI.

	T_C, K	$\overline{N}(E_F)$, States (eV · atom · spin)$^{-1}$	$\overline{\lambda}_{ep}$	$2\Delta(0)/kT_c$	$H_c(0)$, kOe	$H_{c2}(0)$, kOe	$(dH_{c2}/dT)_{T_c}$, kOe/K	$H^*_{c2}(0)$, kOe	$(dH^*_{c2}/dT)_{T_c}$, kOe/K	H_{p0}, kOe
$PbMo_6Se_8$	4.0	0.24	0.82	4.11	0.4	38	32	36	13	74
$SnMo_6Se_8$	3.5	0.20	0.76	2.91	0.2	78	24	38	15	64
$CdMo_6Se_8$	2.4	0.69	0.46	3.66	0.3	–	–	43	26	44
$ZnMo_6Se_8$	2.0	0.25	0.55	–		–	–	–	–	–
$CuMo_6Se_8$	5.9	0.29	0.96	2.95	0.5	100	21	81	20	103
Mo_6Se_8	6.6	0.52	1.20	3.53	1.0	120	23	160	37	116
$Mo_6Se_6Br_2$	6.9	0.55	1.23	3.6	1.1	320	60	199	43	88
$Mo_6Se_6J_2$	4.8	0.59	0.93	–	–	210	58	115	35	88
Mo_6Te_8	–	0.28	0.08	–	–	–	–	–	–	–
$LaMo_6Se_8$	11.6	0.51	1.37	3.95	2.1	445	60	341	43	213

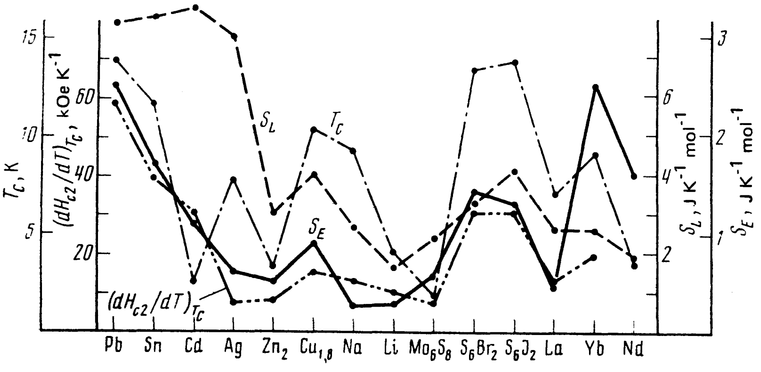

FIG. 3. Comparison of electronic (S_E) and Lattice (S_L) entropies at $T = 20$ K, $(dH_{c2}/dT)_{T_c}$ and T_c for various molybdenum sulfides.

The evaluation of Δ (0) from the temperature dependence of the electronic heat capacity in the superconducting state is not exact, since $C_{es}(T)$ depends strongly on small errors in extrapolating $C_\Delta(T)$ and in determining γ and $C_L(T)$. One cannot, therefore, say with certainty whether the observed non-linear dependence of ln C_{es} on T^{-1} for PbMo$_6$S$_8$ (Ref. 7) is a general property of the MCh's studied or whether it is just a consequence of inaccurate extrapolation, all the more so because a reduction in the coefficient by only 10% gives the usual linear dependence on T^{-1} for all the chalcogenides investigated.[10] The observed departure from linearity can also be produced by the existence of free unpaired electrons. This could indicate that as a result of scattering at $T \to 0$ not all the electrons, which determine the value of γ, go into the "paired" superconducting state. The results of comparing S_E, S_L, T_c and $(dH_{c2}/dt)_{T_c}$ for different molybdenum sulfides are shown in Fig. 3. It can be seen from this figure that the MCh's of the second group have the highest values of these parameters. Comparison of the values of γ obtained from heat capacity measurements with those calculated from the relation $\gamma_H = (2.2 \times 10^{-5}/\rho)(\partial H_{c2}/\partial T)_{T_c}$ shows (Fig. 4) that the linear relation between these quantities is a sufficiently good approximation. At the same time, it can be concluded from comparison of the results in Table I that there is practically no correlation between T_c and γ, λ_{ep} and $N(E_F)$.

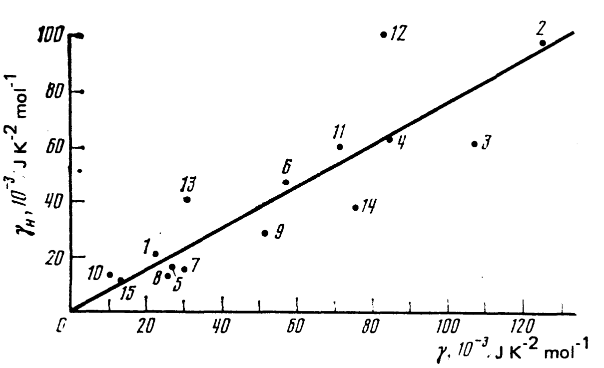

FIG. 4. Dependence of γ_H on γ for molybdenum chalcogenides. The number by each point corresponds to the compound as follows: 1—LaMo$_6$S$_8$, 2—PbMo$_6$S$_8$, 3—SnMo$_6$S$_8$, 4—Sn$_{1.2}$Mo$_6$S$_8$, 5—CdMo$_6$S$_8$, 6—Cd$_{1.2}$Mo$_6$S$_8$, 7—AgMo$_6$S$_8$, 8—Zn$_{1.3}$Mo$_{6.5}$S$_8$, 9—Cu$_{1.8}$Mo$_6$S$_8$, 10—NaMo$_6$S$_8$, 11—Mo$_6$S$_8$Br$_2$, 12—LaMo$_6$Se$_8$, 13—PbMo$_6$Se$_8$, 14—Mo$_6$Se$_8$, 15—LiMo$_6$S$_8$.

DISCUSSION

It has already been pointed out more than once that a number ot TMCh's have a complicated temperature dependence of heat capacity which is not covered by the Debye theory. Their heat capacity can be expressed approximately in the form of the sum of an electronic heat capacity $C_E = \gamma T$ and the lattice part C_L, according to Eq. (2). Studies of the heat capacity of halogen-substituted molybdenum chalcogenides, carried out recently, show that such a treatment of heat capacity can also be applied to these chalcogenides. The results given here enable the electronic heat capacity to be obtained to sufficient accuracy by using the method of calculation employing the expressions derived above, and the magnitudes of the contributions to the lattice part can be determined. This consideration is probably applicable to molybdenum chalcogenides because they are cluster compounds in which the bonds between atoms within a cluster are appreciably stronger than between clusters.

Similar arguments should apparently be applicable to other cluster compounds, for example tungsten bronzes. As noted above, in the analysis of the properties of ternary molybdenum chalcogenides, $C_1(\theta_1)$ can be roughly considered as the contribution described by the Debye function and is associated with translational oscillations of the whole Mo$_6$Ch$_8$ cluster; the term $C_2(\theta_2)$ can be considered as the contribution associated with optic mode oscillations of atoms of the third component, which can be described by the Einstein function. The third term in the expression for the lattice heat capacity only because appreciable at relatively high temperatures ($T > 15$ K). It corresponds to intra-cluster oscillations. The coefficients A_1 and A_2 correspond to the number of three-dimensional oscillators per elementary cell, giving a contribution to the heat capacity components C_1 and C_2. When binary MCh's are considered, the second term in the expression for C_L can be related to torsional oscillations of the cluster.

It could be concluded from the discussion of heat capacity given, that changing the mass of atom A in A$_x$ Mo$_6$Ch$_8$ or the mass of the Mo$_6$Ch$_8$ cluster should lead to a change in oscillation frequency proportional to $M_A^{-1/2}$. If we try to determine the change in frequency from the experimental results, it appears that an accurate correlation is not observed between θ_2 and the mass of atom A for ternary molybdenum sulfides. In fact, $\theta_2 = 48$ K for PbMo$_6$S$_8$ and $\theta_2 =$ K for SnMo$_6$S$_8$; the ratio $(\theta_2)_{Pb}/(\theta_2)_{Sn} = 1.17$ while

$(M_{\mathrm{Sn}}/M_{\mathrm{Pb}})^{1/2} = 0.76$. Such a 35% discrepancy is probably a result of a change in binding strength of atom A on substituting Pb for Sn. A change in the volume of the elementary cell[39] and the nature of such a change can be different in Chevrel-phases of the 1st and 2nd groups. The mangitude of θ_1 for TMCh's should remain constant for all sulfides, independent of which metal A is in the compound. In fact θ_1 does not stay constant although its variation is relatively small, especially for 2nd group Chevrel-phases, i.e., for molybdenum chalcogenides with Pb, Sn, Ag. Changing metal A in this case probably leads to a small change in the force binding the clusters of the lattice. A fairly close relation between θ_2 and $M^{1/2}$ is observed for halogen-substituted molybdenum selenides if the mass of the cluster is taken for M. In spite of the departures noted from the simplified assumptions about TMCh's in the form of quasi-binary compounds, one component of which is metal A, while the other is the $\mathrm{Mo_6Ch_8}$ cluster, it should be pointed out that the model is convenient for discussing the properties of TMCh's. No doubt, its further development will not only lead to a better agreement between the model and experiment, but will enable new properties of cluster systems to be predicted.

It must be pointed out in a discussion of model representations of molybdenum chalcogenides that the low-frequency contribution to the heat capacity of the optic modes of oscillation of the atoms of the third component only show up clearly in the 2nd group Chevrel-phases, for example in $\mathrm{SnMo_6S_8}$ and $\mathrm{PbMo_6S_8}$ in which heavy atoms with relatively large atomic radius figure as the third component. For 1st group Chevrel-phases which have light, relatively small atoms A, their optic vibrations are probably in the higher frequency range, so that the $C_p(T)$ dependence at low temperatures differs little from cubic. In addition, the groups of atoms A in 1st group Chevrel-phases are shifted from the [0,0,0] positions and, distinct from 2nd group Chevrel-phases, their position in the lattice can be represented approximately as [0,0,½]. They are more strongly bonded to the cluster and probably exert a stronger influence on oscillation of the cluster itself. Atoms A in compounds $\mathrm{A}_x\mathrm{Mo_6S_8}$ also have an influence on the magnitude of γ. For example, in molybdenum sulfides with low-frequency optic modes, i.e., in 2nd group Chevrel-phases, γ has a relatively higher value than could be connected with the large electron-phonon interaction. In 1st group Chevrel-phases, except for $\mathrm{Cu_{1.8}}$-$\mathrm{Mo_6S_8}$, γ is small. The reason for the relatively high value of γ for $\lambda_{\mathrm{ep}}\mathrm{Mo_6S_8}$ is not quite clear. It is not impossible that in this compound there is a lattice contribution, linearly dependent on temperature related, for example, to the large anharmonicity or to the presence of a quasi-amorphous phase, which is to some extent confirmed by the difference between results for C_L and the phonon spectrum (Fig. 3). If results on sulfides and selenides are compared, it can be noted that relatively large values of γ for selenides (but smaller than for sulfides) are only observed in compounds with rare earths.

The influence of the third component on the properties of superconducting TMCh's was noted earlier.[2] It followed from the results given there that the dependence of C_L on the atomic weight of atom A in $\mathrm{AMo_6S_8}$ appeared to be a smooth function for atoms A lying in one column of the periodic table, i.e., having as a rule, the same valency. It was shown later, when studying the isotope effect,[40] that in the case of $\mathrm{SnMo_6S_8}$, the dependence of T_c on the mass of the Sn atom is an increasing one: T_c increases as the mass of the Sn isotope increases, i.e., there is an anomalous isotope effect (see also Ref. 41). The anomalous isotope effect for Sn may be a result of the large anharmonicity of the Sn optic modes. As has been noted.[42] it is just the optic modes which can lead to large values of λ_{ep}. On the other hand, charge transfer from A to the $\mathrm{Mo_6S_8}$ cluster takes place; this process is determined by the valency of atom A. The change in the density of states is probably related to just this process. It can, therefore, be assumed that the change in transition temperature on changing A comes about from changes in both $N(E_F)$ and λ_{ep}. Both factors (changes in $N(E_F)$ and λ_{ep}) will be important for TMCh's of the second group, i.e., for heavy A, while changes in $N(E_F)$ are more important for TMCh's of the first group. On changing the chalcogenide, the lattice parameters and the binding forces in the cluster change, and this can complicate the picture appreciably.

As is well known,[2] the main feature of TMCh's is their high critical magnetic field H_{c2}. In order to consider the relation between the TMCh parameters, obtained from heat capacity measurements, and the magnitude of the upper critical field, we can write the expression for the temperature dependence of H_{c2} in the form[43]

$$H_{c2}(T) = H_{c2}{}^{*}(T) -- 0.22(\alpha/\lambda_{So})\,T_c H_{c2}{}^{2}(T).$$

The first term in this formula, $H^*_{c2}(T)$, is the orbital critical field and the second represents the interaction between the external field and the spin of the conduction electrons. In the expression given, α is the Maki parameter and λ_{so} is the spin-orbit interaction parameter. Near T_c the field H^*_{c2} is nearly equal to H_{c2}, so that we can take $(dH_{c2}/dT)_{T_c} = (dH^*_{c2}/dT)_{T_c}$. If we look at the dependence of the experimental values of $(dH^*_{c2}/dT)_{T_c}$ on γ derived from measurement of heat capacity, it can be seen that a monotonic relation exists between these quantities. Since $\gamma = \gamma_0(1+\lambda_{\mathrm{ep}})$ and $\gamma_0 \sim N(E_F)$, it can be thought that the critical magnetic fields of MCh's should depend on $N(0)$ and on λ_{ep}. This means that the details of the phonon spectra of MCh's influence H_{c2} through λ_{ep}. Experimental values of H_{c2} and calculated values of $H_{c2}(0)$ are shown in Tables IV and VI, together with their temperature derivatives. The good agreement between values of $H_{c2}(0)$ and $H^*_{c2}(0)$ (especially if we take into account the fact that the difference between experimental values of $H_{c2}(0)$ given by different authors reaches 20%) can be considered to be a consequence of the spin-orbit interaction constant being very high in the compounds studied, so that the second term in the expression of H_{c2} at $T=0$ is small. This conclusion is most valid for 2nd group Chevrel-phases for which H_{c2} exceeds the paramagnetic limit. As is well known, 2nd group Chevrel-phases, expecially $\mathrm{PbMo_6S_8}$ have fairly high values of the critical current density J_c as well as high critical fields.[2] At first sight it is difficult to reconcile the high values of critical current densities with high critical magnetic fields since the critical paired current must depend directly on the relaxation time τ or the mean free path l of the carriers, while the orbital critical field should be inversely proportional to l. The large J_c and H_{c2} can be reconciled if it is accepted that the systems studies have high densities of state at the Fermi surface, $N(E_F)$. Results obtained from measurements of heat capacity confirm this point of view.

In conclusion it should be pointed out that the discussion of the properties of MCh's which has been presented and the model representations used for describing these properties could, in their further development, be applicable not only for MCh's but for other superconducting compounds of the cluster type.

We are grateful to A. V. Mitin for his part in the discussion of the results and for help in preparing this article.

[1)] It should be pointed out that superconducting compounds are known which contain no metallic atoms: SN_x and even some organic superconductors.[1]

[2)] Determination of x was carried out by x-ray fluorescence analysis. The phase composition was determined by x-ray diffraction.

[3)] Most of the measurements in steady magnetic fields were carried out in the International Laboratory of High Magnetic Fields and Low Temperatures (Wroclaw, Poland).

[4)] For pure MCh's the susceptibility is usually paramagnetic (only MCh's with chalcogenide metals are an exception) and depends weakly on temperature. It can be represented in the form $\chi = \chi_0 + C/(T - \theta)$. On the assumption that χ_0 is mainly determined by the Pauli susceptibility, we can determine $\gamma_x = (\pi^2/3)(k_B/\mu_B)\chi_0$. We should remark, however, that there is insufficient basis for such an assumption.

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Translated by R. Berman