The specific heat of the magnetic superconductors $NdMo_6S_8$ and $NdMo_6Se_8$ at low temperatures

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The specific heats of $NdMo_6S_8$ and $NdMo_6Se_8$ have been measured at temperatures between 1.8 and 30 K. Lambda-type anomalies were observed at 1.93 and 2.3 K respectively. Possible reasons for such anomalies are discussed.

1. INTRODUCTION

The study of the mutual influence of two quantum cooperative phenomena—superconductivity and magnetism—has aroused great interest since the late 50s.[1] Superconductors with a small amount of magnetic impurity, randomly distributed in an initially superconducting matrix, were studied originally. However, appreciable progress was achieved as studies were undertaken of so-called magnetic superconductors in which the magnetic ions form a regular sublattice in the crystal structure (see, for example, the review of Ref. 20). Superconductivity in compounds with a regular sublattice of magnetic ions was relatively recently found in some materials belonging mainly to two classes of ternary rare earth cluster compounds, ternary molybdenum chalcogenides $REMo_6X_8$ (Refs. 3 and 4) (RE is a rare earth, $X = S$, Se) and ternary rhodium borides $RERh_4B_4$ (Ref. 5). The existence of superconductivity in these compounds in spite of the very considerable magnetic ion content (7 and 11% respectively) is associated with the anomalously small value of the exchange interaction between the conduction electrons and the localized magnetic moments of the rare earth ions.[1)] [2] The regular distribution of magnetic ions in the compounds $REMo_6X_8$ and $RERh_4B_4$ makes it possible to avoid the difficulties met in studies of systems with magnetic impurities; the absence of a single phase, clusterings of magnetic ions and the transition of the magnetic subsystem to a state of the spin glass type.

It was established by neutron scattering studies of magnetic suprconductors that the rare earth sublattice goes into a magnetically ordered state at a temperature $T_m \approx (0.1–1)$ K, which lies below the temperature T_c of the superconducting transition.[2] It appeared that the transition to the ferromagnetically ordered state results in the destruction of superconductivity, with a possible coexistence of superconductivity and an inhomogeneous magnetic order near the ferromagnetic transition temperature. At the same time, the transition to an antiferromagnetically ordered state does not destroy superconductivity but causes anomalies to appear in the temperature dependence of the upper critical field $H_{c2}(T)$, the specific heat $C(T)$ and of the magnetic susceptibility $\chi(T)$. (The preservation of superconductivity on antiferromagnetic ordering is associated with the fact that the exchange and magnetic fields, which oscillate rapidly on an atomic scale, give values close to zero when averaged over the coherence length).

In work on measurements of the specific heat of magnetic superconductors, apart from features corresponding in temperature to transitions to the superconducting and magnetically ordered states, λ anomalies were found in the superconducting state ($T_m < T_\lambda < T_c$).[8,9] In the present work we report the finding of similar anomalies in the temperature dependence of the specific heat of the compounds $NdMo_6S_8$ and $NdMo_6Se_8$.

Superconductivity was found in the compounds $NdMo_6S_8$ and $NdMo_6Se_8$ by Fischer *et al.*[3] and Shelton *et al.*,[4] the values of T_c being 3.5 and 8.2 K respectively. the transition to the antiferromagnetically ordered state for $NdMo_6S_8$ at $T_m \approx 0.3$ K was found by Alekseevskiĭ and Narozhnyĭ[10] from anomalies in the $H_{c2}(T)$ dependence. Measurements under pressure[11] showed that T_m increases appreciably on the application of pressure ($\partial T_m / \partial P = 2.5 \times 10^{-5}$ K·bar^{-1}). This in turn enabled the dominant contribution of exchange interaction in establishing magnetic order in these systems to be determined,[11] and the amplification of the exchange interaction under pressure, similar to that observed for the Chevrel phases with iron as magnetic impurity $Fe_xSnMo_6S_8$ (Ref. 7), to be established.

THE EXPERIMENTS

The measurements of specific heat were carried out in a calorimeter with a mechanical heat switch[12] over the temperature range 1.8–30 K. The specific heat in a magnetic field was measured in an apparatus described earlier.[2)] [13] A standard copper specimen from the Argonne National Laboratory was used for calibration.The accuracy in measuring specific heat was better than 2%. The magnetic susceptibility was measured on a magnetic balance in a field $H = 4.25$ kOe at temperatures from 6 to 300 K. The specimens were prepared in the same way as described earlier.[10]

RESULTS

The superconducting transition temperature determined from resistance measurements was 3.4 and 8.3 K for specimens of $NdMo_6S_8$ and $NdMo_6Se_8$ respectively.The feature in the specific heat near T_c for $NdMo_6S_8$ is clearly visible; see Fig. 1. However, a λ-like anomaly is clearly seen in the $C(T)$ plot at a lower temperature. The temperature of the maximum specific heat $T_\lambda = 1.93$ K.

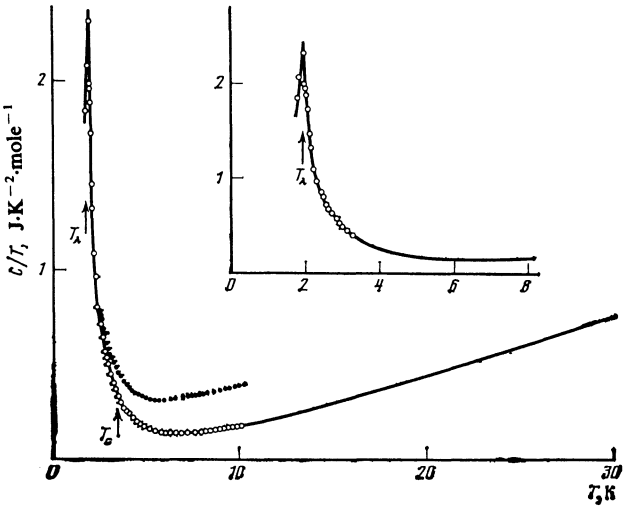

FIG. 1. The dependence of C/T on the temperature T for $NdMo_6S_8$. The experimental points are not shown for temperatures above 10 K: O) $H=0$, ●) $H=50$ kOe.

The experimentally observed $C(T)$ relation at temperatures 10 K$\leqslant T \leqslant$25 K can be approximately described by the relation $C(T) = \gamma T + \beta T^3$. This can be considered as evidence of the small contribution to the specific heat of $NdMo_6S_8$ of optical Einstein phonon modes, which show up clearly in the specific heat of, for example, $SnMo_6S_8$ and $PbMo_6S_8$ (Ref. 14). The small contribution of Einstein modes, in turn, can be associated with the stronger binding of the RE^{3+} ions to the molybdenum chalcogenide lattice compared with Pb^{2+} and Sn^{2+} ions.

The coefficient of the electronic specific heat γ, determined by extrapolation to $T=0$, is 75 mJ·K^{-2} mole^{-1}. An estimate of the "excess" contribution to the entropy due to the λ anomaly, S_λ, can be obtained by integrating the quantity $[C(T) - \gamma T - \beta T^3]\cdot T^{-1}$. The value of S_λ for $NdMo_6S_8$ was then about 2.6 J·K^{-1} mole^{-1}.

Measurements of the specific heat of $NdMo_6S_8$ in a magnetic field of 50 kOe showed that the λ anomaly broadens somewhat and the additional contributions to the specific heat for $T > T_\lambda$ increases appreciably. A similar magnetic field effect was observed earlier[15] on the λ anomaly for $YbMo_6S_8$.

The jump in the specific heat of $NdMo_6S_8$ at the superconducting transition is clearly marked (see Fig. 2). As for neodymium molybdenum sulfide, a λ anomaly is observed in the $C(T)$ curve for $NdMo_6Se_8$ at $T_\lambda = 2.3$ K. An estimate of the excess entropy associated with the λ anomaly gives the value $S_\lambda \approx 1.7$ J·K^{-1} mole^{-1}.

The results of measuring the temperature dependence of the magnetic susceptibility $\chi(T)$ for $NdMo_6S_8$ are shown in Fig. 3. The observed $\chi(T)$ relation between 70 and 300 K is well described by the Curie-Weiss law $\chi(T) = C_q(T+\Theta)$. The value of the Curie-Weiss temperature Θ and the effective magnetic moment μ_{eff}, determined from the high-temperature ($T > 70$ K) $\chi(T)$ dependence, are then respectively 28 K and 3.7 μ_B, which agrees well with the results of Pellizzone *et al.*[16] The value of the effective magnetic moment $\mu_{\text{eff}} = 3.7\,\mu_B$ is close to the theoretical value for the free Nd^{3+} ion ($3.62\,\mu_B$). (The small difference may be associated with the insignificant departure from stoichiometry of the composition of the specimens, corresponding in fact to a composition $Nd_{1.06}Mo_6S_8$.)

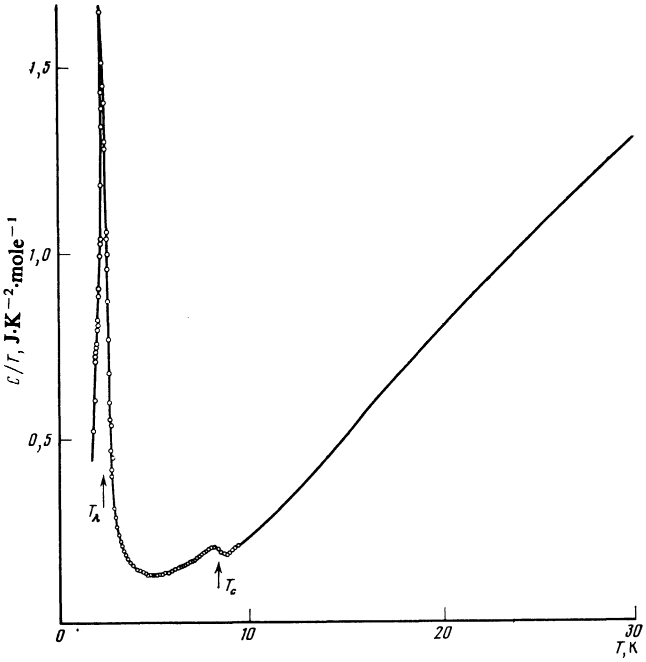

FIG. 2. The dependence of C/T on the temperature T for $NdMo_6Se_8$. The experimental points are not shown for temperatures above 10 K.

At the same time a marked departure of the $\chi(T)$ curve from the Curie-Weiss law is observed for temperatures $T < 70$ K, corresponding to a reduction in the effective mag-

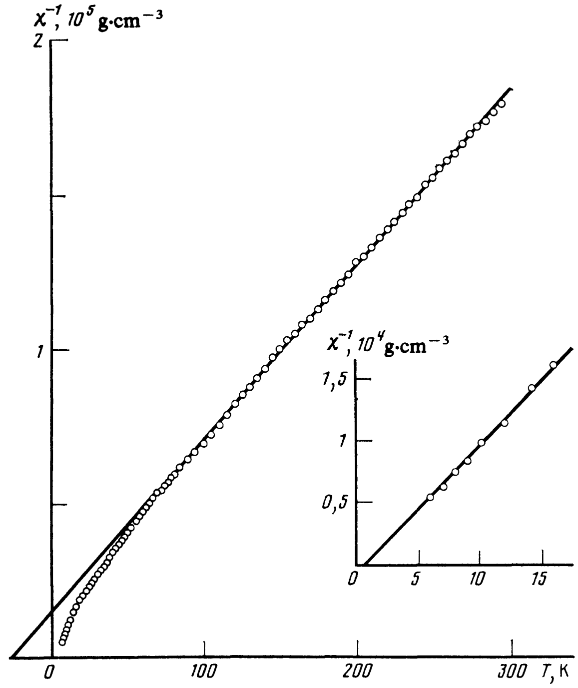

FIG. 3. The temperature dependence of the reciprocal of the magnetic susceptibility of $NdMo_6S_8$.

netic moment and modulus of the Curie-Weiss temperature. The "low-temperature" value of Θ_{LT} determined by extrapolation of the $\chi^{-1}(T)$ plot in the temperature range 6–16 K is then 0 ± 1 K.

The nonlinear $\chi^{-1}(T)$ dependence for rare earth molybdenum chalcogenides with RE = Tb, Er, Dy, and Ho has been remarked on before.[16,17] In view of the fact that the $\chi^{-1}(T)$ dependence for the compounds $GdMo_6S_8$ and $GdMo_6Se_8$ with the Gd^{3+} ion, for which there is no orbital moment, is practically linear in the temperature range 1–300 K, while the value of $|\Theta|$ is below 2 K (Refs. 16, 17), the nonlinear $\chi^{-1}(T)$ dependence observed for $NdMo_6S_8$ can evidently be explained by crystal field effects.

DISCUSSION

The value of the excess entropy associated with the anomalies, found in $NdMo_6S_8$ and $NdMo_6Se_8$, amounts respectively to 46 and 30% of the value of $R \ln(2S+1) = R \ln 2 = 5.68$ $J \cdot K^{-1}$ $mole^{-1}$ which would rise on complete magnetic ordering on the assumption that the ground state of the Nd^{3+} ion in the crystal field of the molybdenum chalcogenides is a doublet.[18] The appreciable value of the excess entropy S_λ practically excludes the possibility of explaining the observed λ anomalies by the presence of impurity phases.

It should also be noted that because of the large value of the excess entropy ($\sim 32\%$), the suggestion of explaining the λ anomaly in the specific heat of $YbMo_6S_8$, observed earlier,[8,15] by the presence of ytterbium oxysulfide impurity, propounded by Jorgensen *et al.*[19] cannot be considered convincing. According to Alekseevskiĭ *et al.*[15] the amount of impurity phases in $YbMo_6S_8$, which contain Yb, was less than 1%. Besides, it must be remarked that the hydrogen treatment used by Jorgensen *et al.*[19] can produce an appreciable change in magnetic properties of the compounds obtained similar, for example, to what occurs in the case of palladium hydrides.[3)]

The nature of the λ anomaly in the specific heat of rare earth molybdenum chalcogenides cannot be considered to be completely explained. While for $GdMo_6Se_8$ (Ref. 9) and $NdMo_6S_8 T_m < T_\lambda < T_c$, a similar λ anomaly is observed for $DyMo_6S_8$ at $T_\lambda = 4.5$ K $> T_c$ (Ref. 21). These anomalies are clearly associated with the presence of the RE magnetic ions. As has been noted by McCallum *et al.*[9] and Woolf *et al.*,[21] there are no anomalies in $C(T)$ for the corresponding nonmagnetic compounds $LaMo_6X_8$ and $LuMo_6X_8$. However, the λ anomalies under discussion are evidently not associated with magnetic orders of the RE ions. Antiferromagnetic ordering in the Gd, Nd, and Dy sublattices occurs at lower temperatures: 1, 0.3 and 0.4 K respectively. It should also be pointed out that the temperature dependence of the upper critical field for $NdMo_6S_8$ with $T_\lambda = 1.93$ K has no singularities[4)] (see Fig. 4). Besides, as was shown[22] in studying the quasibinary layer $(La_{1-x}Gd_x)Mo_6Se_8$, the value of T_λ and the Curie-Weiss temperature Θ are practically independent of Gd concentration. This evidently points to a local nature of the λ anomaly observed for it.

As was shown by the results of the x-ray diffraction analysis and neutron scattering, carried out on a series of rare earth molybdenum chalcogenides at temperatures both above and below T_λ, these compounds do not undergo structural transformations at temperatures below room temperature (e.g. Refs. 2, 22).

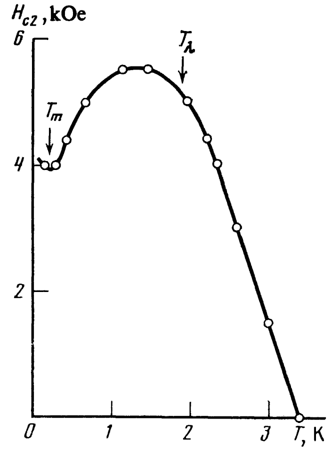

FIG. 4. The dependence of the upper critical magnetic field H_{c2} on temperature for $NdMo_6S_8$

The presence of magnetic rare earth ions is thus essential for the appearance of λ anomalies in molybdenum chalcogenides, but these anomalies are associated with neither magnetic ordering in the RE ion sublattices nor structural transformations at $T = T_\lambda$.

It is possible that the observed λ anomalies could be associated with the complicated character of the energy levels of the RE^{3+} ions in the crystal field of the chalcogenides, which can give rise to singularities of the Schottky type. It should be pointed out in this connection that a λ type anomaly in the $C(T)$ variation has been observed in metallic neodymium at $T_\lambda = 7.4$ K and has been related to the appearance of a modified Schottky effect on the level of the Nd^{3+} ion with $J = 9/2$ which is split in the crystal field.[18] At the same time, crystal field effects for $NdMo_6S_8$ are clearly seen from the results of measuring the magnetic susceptibility (see Fig. 3).

It is also possible that the $REMo_6X_8$ compounds minor readjustment of the electronic spectrum of these compounds can produce the λ anomalies in the specific heat, similar to the possibility noted by McCallum *et al.*[22] Further investigations of magnetic superconductors will help to establish the true nature of the λ anomalies found.

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[1)]The introduction of about 1% of magnetic ions usually leads to the complete suppression of superconductivity.[6] For example, the critical concentration of iron for the molybdenum chalcogenide $SnMo_6S_8$ is only 0.41 at. % and the value of the exchange integral has a value of 0.31 eV as distinct from $ReMo_6X_8$ (Ref. 7).

[2)]Measurements of specific heat and magnetic susceptibility were carried out in the International Laboratory for High Magnetic Fields and Low Temperatures, Wroclaw, Poland.

[3)]A study of hydrogen-containing molybdenum chalcogenides has been carried out, for example, by Alekseevskiĭ *et al.*[20]

[4)]The possibility of explaining the λ anomaly in the specific heat observed for $YbMo_6S_8$ by a magnetic transition at $T = T_\lambda$ cannot be ruled out. The absence of singularities on the $H_{c2}(T)$ plot at $T = T_\lambda$ may be associated with the relatively large value of the upper critical fields for this compound, $H_{c2}(0) \approx 150$ kOe.

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