Distinctive features of the temperature dependence of the Pauli contribution to the magnetic susceptibility of $SnMo_6Se_8$ and Mo_6Se_8; NMR data for ^{119}Sn, ^{77}Se, and ^{95}Mo

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The behavior of the magnetic susceptibility, of the Knight shift, and of the rate of spin-lattice relaxation of the nuclei ^{95}Mo, ^{119}Se, and ^{77}Se in the Chevrel-phase-structure superconducting compounds Mo_6Se_8 ($T_c = 6.7$ K) and $SnMo_6Se_8$ ($T_c = 3.5$ K) is investigated in the temperature range 4–500 K. The spin contribution to the magnetic susceptibility of the *d*-band electrons is separated by a joint analysis of the data. Possible causes of the presence of maxima on the temperature dependences of the susceptibility and of the NMR parameters of the investigated compounds are also discussed.

INTRODUCTION

The superconductors $SnMo_6Se_8$ ($T_c \approx 3.5$ K), Mo_6Se_8 ($T_c \approx 6.5$ K) are compounds with Chevrel phase structure MMo_6X_8, which are intensively studied at the present time and have rhombohedral crystal-lattice symmetry (space group $R\bar{3}$).[1,2] In the superconducting compound $SnMo_6S_8$ of this class, with a superconducting transition temperature that can reach 14 K, the density of states on the Fermi level is, according to specific-heat data[3] and NMR data,[4,5] quite high $(N0) \approx 1.0$ $[\text{eV}\cdot(\text{Mo atom})\cdot\text{spin}]^{-1}$ and is made up mainly of the 4*d* states of the molybdenum atoms with e_g-orbital symmetry. The temperature dependences of the Knight shift and of the spin-lattice relaxation time T_1 of ^{95}Mo in this system are determined by the temperature dependence of the Pauli contribution of the *d*-band. The Knight shift and $(T_1T)^{-1}$ of the ^{119}Sn nuclei are proportional to χ_d, apparently as a result of hybridization of the tin and molybdenum states on the Fermi level in this compound. These conclusions are confirmed by the results of band calculations,[1] where it is shown that in this system the Fermi level is located close to the peak of the density of the molybdenum *d*-states. The values of $N(0)$ given in Ref. 1 are close to the experimental estimates.

The situation for compounds based on selenium is less definite. According to low-temperature specific-heat data the density of states on the Fermi levels of $SnMo_6Se_8$ and Mo_6Se_8 is much lower compared with $SnMo_6S_8$. This is probably one of the reasons for the lower superconducting-transition temperatures of selenides. The available band calculations, however, lead to values comparable with the density of states of $SnMo_6S_8$, viz., $N(0) = 0.85$ to 0.92 and 0.8 to 1.0 $[\text{eV}\cdot(\text{Mo atom})\cdot\text{spin}]^{-1}$ for $SnMo_6S_8$ and Mo_6Se_8, respectively.[1] It is therefore definitely of interest to investigate the magnetic susceptibility and NMR in these systems in a wide range of temperatures, in order to separate the Pauli contribution to χ and to determine the character of its temperature dependence, so as to estimate $N(0)$ for various temperatures. Continuing an earlier study[5] of the features of the electronic structure of ternary molybdenum chalcogenides, we have investigated the magnetic susceptibility and NMR of the nuclei ^{95}Mo, ^{77}Se and ^{119}Sn in the compounds Mo_6Se_8 and $SnMo_6Se_8$.

EXPERIMENTAL RESULTS

The $SnMo_6Se_8$ sample was obtained by synthesis in an ampul, similar to that described in Ref. 5, followed by annealing at $T = 950$ °C for 24 hours. The binary selenide Mo_6Se_8 was prepared in powdered form in accordance with Ref. 6. The synthesis was at a temperature close to 1100 °C. Stagewise annealing and intermediate remixing of the products, together with constant x-ray diffraction monitoring of the phase composition, have made it possible to synthesize an almost single-phase sample. The structural and superconducting properties of the samples are listed in the table, which contains also the results of activation and atomic-absorption analysis of the content c_{Fe} of the iron-atom admixture.

It should be noted that annealing of $SnMo_6Se_8$ at higher temperature, $T_{ann} = 1150$ °C for 20 h, raised the critical superconducting transition temperature T_c to 7 K, the transition being stretched out at lower temperatures. A similar value of T_c for $SnMo_6Se_8$ was attributed in Ref. 7 to the existence of a high-temperature structural modification of this system. Comparison of the NMR spectra of ^{77}Se in Mo_6Se_8 and $SnMo_6Se_8$ ($T_c = 3.5$ K) and in the $SnMo_6Se_8$ sample ($T_{ann} = 1150$ °C) pointed to another explanation of the observed rise of the critical temperature on annealing. The spectrum of the sample annealed at 1150 °C contains two NMR lines of ^{77}Se, with intensity ratio 1:2, corresponding to the positions of the lines of the binary compound and $SnMo_6Se_8$ ($T_c = 3.5$ K). X-ray diffraction analysis of this sample, which disclosed the presence of the (223) and (015) reflections corresponding to the Mo_6Se_8 phase, confirmed the assumed phase stratification of the molybdenum selenide $SnMo_6Se_8$ at this annealing temperature.

The measurement of the magnetic susceptibility, the NMR experiments, and the reduction of the data are described in detail in Ref. 5. The ^{77}Se NMR line shift of the samples was determined from the position of the absorption-line maximum relative to the ^{77}Se NMR signal of a selenium solution in a (1:1) mixture of nitric and hydrochloric acid, viz., $(\gamma/2\pi) = 812.99$ Hz/Oe.

Figure 1 shows the temperature dependences of the magnetic susceptibility of the investigated samples. The growth of χ at low temperatures is due to the presence of a

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TABLE I.

Compound	$SnMo_6Se_8$	Mo_6Se_8
a_H	9.510(5)	9,562(5)
c_H, A	11,845(5)	11.180(5)
T_c, K	3.50(15)	6.7(2)
c_{Fe} (performance)	0.018	0,035
χ_{dia}	−4.35	−4.05
χ_s	0.09(2)	<0.03
χ_{orb} 10^{-4} cm³/mol	3.75(30)	3.25(30)
χ_{max},	4.6(3) (300 K)	5.9(3) (150 K)
χ_d $(T>T_c)$	3.6(3) (4,2 K)	4.9(3) (10 K)
$(T_1T)_s^{-1}$ (Mo), $s^{-1}\cdot K^{-1}$	0.015	0.01
K_0(Se)	−0,0004	−0.0004
K_0(Sn)	0.0025(6)	
K_s(Mo)	0.0003	<0.0002
K_{orb}(Mo)	0.0035	0,0025
$N(0)$, $(eV\cdot at.Mo\cdot spin)^{-1}$	0.8 (300 K) 0.6(4,2 K)	0.95 (150 K) 0.80 (10 K)

small iron impurity in the initial molybdenum. Using the c_{Fe} analysis data and recognizing that at low densities the magnetic moment of the impurity atoms is $\mu_{Fe} = 4.0\mu_B$ in these systems, we can subtract the impurity contribution and determine more accurately the behavior of the magnetic susceptibility in the low-temperature region. The error is due mainly to inaccurate allowance for the impurity contribution to χ. The low temperature part of the $\chi(T)$ curve for $SnMo_6Se_8$ duplicates the qualitatively the temperature dependence of the magnetic susceptibility of $PbMo_6Se_8$ (Ref. 8). Attention is called to the nonmonotonic temperature dependence, typical of both selenides, of the magnetic susceptibility. The maximum for the binary compound is reached in the $T \sim 150$ K region, and goes to room temperature for the ternary selenide $SnMo_6Se_8$. All this gives grounds for concluding that the earlier estimates of the densities of the electronic states, based on χ observed at room temperature, require a detailed review. For comparison, Fig. 1 shows the temperature dependence of the magnetic susceptibility of $SnMo_6Se_8$ ($T_c = 11.5$ K), showing a slowing down of the growth of χ at $T < 100$ K; according to the data of Ref. 9, the samples have in this temperature region a maximum with $T_c = 14$ K. The nonmonotonic behavior of the magnetic susceptibility in $PbMo_6S_8$ and $SnMo_6S_8$ at $T < 100$ K is attributed at present to the low-temperature instability of these compounds.[10] There are no corresponding data for selenides.

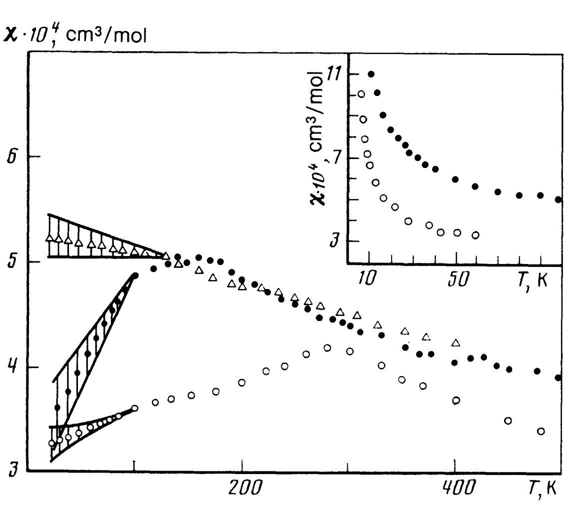

FIG. 1. Temperature dependences of the magnetic susceptibilities of $SnMo_6Se_8$(○), Mo_6Se_8 (●), $SnMo_6Se_8$ (△) (Ref. 5). The vertical lines show the error in the low-temperature region.

A nonmonotonic behavior is observed also in the temperature dependences of the Knight shift K and of the value of $(T_1T)^{-1}$ for the ^{77}Se nuclei in the investigated selenide samples (Fig. 2). At helium temperature the values of $(T_1)_{Se}$ for $SnMo_6Se_8$ ar close to those published in Ref. 11. The differences between the values of K_{Se} are apparently due to an inaccurate determination, in Ref. 11, of the position of the ^{77}Se NMR line in the diamagnetic sample. In contrast to the conclusion drawn in Ref. 11, that K_{Se} and $(T_1T)_{Se}^{-1}$ are independent of temperature, our data point to a correlation between the temperature dependences of these quantities and the magnetic susceptibility. This is particularly pronounced at temperatures above 100 K, where the influence of the error due to subtracting the impurity contribution to the magnetic susceptibility is negligibly small.

The ^{77}Se NMR line in $SnMo_6Se_8$ and Mo_6Se_8 is inhomogeneously broadened, a feature of the Knight-shift distribution for the selenium nuclei of the samples. The linewidth in $SnMo_6Se_8$ increases somewhat with decrease of temperature: $\delta H(300\,K) = 11.7(4)$ Oe; $\delta H\,(5\,K) = 13.0(4)$ Oe (at 16.7 MHz). In a binary compound the ^{77}Se NMR line is asymmetric and is more gently sloping towards the weaker fields. The linewidth in Mo_6Se_8 is substantially larger than in the ternary tin selenide and is constant, within the limit of the errors, in the investigated temperature interval, $\delta H(150\,K) \approx \delta H\,(10\,K) = 43(3)$ Oe (at 16.7 MHz). The homogeneous broadening of the lines is characterized by a spin-spin relaxation time T_2 whose length for Mo_6Se_8 and $SnMo_6Se_8$ is independent of temperature: $T_2(SnMo_6Se_8) = 5.0(5)$ ms and $T_2(Mo_6Se_8) = 4.0(5)$ ms.

Just as for the Knight shift, the value of $(T_1T)^{-1/2}$ of the ^{119}Sn nuclei of $SnMo_6Se_8$ decreases with temperature (Fig. 3). The values of K_{Sn} and $(T_1T)_{Sn}^{-1/2}$ also correlate with the magnetic susceptibility. An additional line Sn2 was observed[5] in the NMR spectra of ^{119}Sn in $SnMo_6Se_8$, attesting to the presence of magnetically nonequivalent positions of the tin atoms in the structure of this compound. There is

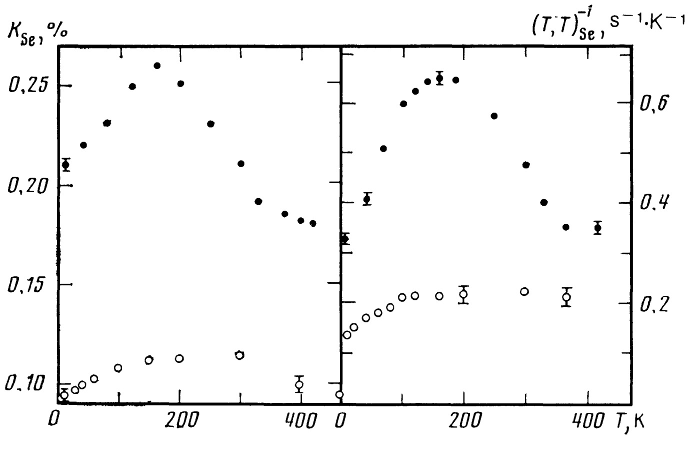

FIG. 2. Temperature dependences of the Knight shift K_{Se} and of $(T_1T)^{-1}_{Se}$ of ^{77}Se nuclei in SnMo$_6$Se$_8$ (○) and Mo$_6$Se$_8$ (●).

apparently no such nonequivalence of the tin atom positions in the ternary selenide. After substracting the ^{119}Sn NMR line of the metallic-tin phase (β-Sn) present in the investigated spectrum, the NMR spectrum of ^{119}Dn in SnMo$_6$Se$_8$ constitutes a single inhomogeneously broadened symmetric line with a positive Knight shift. In analogy with the ^{77}Se NMR line, the ^{119}Sn linewidth due to the distribution of the Knight shifts in the sample increases insignificantly with decrease of temperature $\delta H(300\ \text{K}) = 23.0(5)$ Oe and $\delta H(5\ \text{K}) = 26.0(5)$ Oe (at 32.3 MHz). The observed broadening is substantially smaller than that occurring in the same temperature interval for SnMo$_6$S$_8$ (Refs. 4 and 5), owing apparently to the lower values of K_{sn} in the ternary selenide.

Figure 4 shows the experimental values of the isotropic component of the Knight shift K_{iso} and of the value of $(T_1T)^{-1/2}$ of the ^{95}Mo nuclei in the compounds SnMo$_6$Se$_8$ and Mo$_6$Se$_8$. The variation of these quantities duplicates the main features of χ of the compounds below room temperature. The anisotropic component is independent of temperature within the limit of errors: K_{ax}(SnMo$_6$Se$_8$) $= -0.05(2)\%$, K_{ax}(Mo$_6$Se$_8$) $= -0.06(2)\%$. The Knight-shift anisotropy for these compounds was found in Ref. 5 to have the same sign as K_{ax} for SnMo$_6$S$_8$ by separating a temperature-dependent component proportional to the magnetic susceptibility and due to the spin-dipole interaction between the conduction-band 4d electrons and the magnetic moment of the moybdenum-atom nucleus. Below room temperature for SnMo$_6$Se$_8$ (and at $T < 150$ K for Mo$_6$Se$_8$) we have $dK_{iso}/dT < 0$. In the superconducting state, the Knight shift of ^{95}Mo in the binary compound increases by 0.06%.

DISCUSSION OF RESULTS

In our preceding paper[5] we separated the contributions to the magnetic susceptibility of SnMo$_6$S$_8$ by a joint analysis of the ^{95}Mo NMR data in the "tight binding" approximation for the d-band electrons with allowance for the symmetry of the nearest surrounding of the molybdenum atoms. It was assumed that χ consists of the following main components: the diamagnetic susceptibility χ_{dia} of the ion cores, the Pauli susceptibilities χ_s and χ_d of the S- and d-band electrons, and the Van Vleck susceptibility χ_{orb} of the d electrons:

$$\chi=\chi_{dia}+{}^{2}/_{3}\chi_{s}+\chi_{orb}+\chi_{d}, \qquad (1)$$

where χ_{dia} and χ_s are independent of temperature. The temperature dependence of the magnetic susceptibility is determined predominantly by the Pauli contribution χ_d, apparently as a result of the proximity of the Fermi level to the singularities of the d-state density function in this compound.

In our opinion, the data on the Knight shift and on the rate of the spin-lattice relaxation of the ^{95}Mo nuclei in SnMo$_6$Se$_8$ and MoSe$_8$ permit an analogous conclusion to be drawn concerning the cause of the temperature dependence

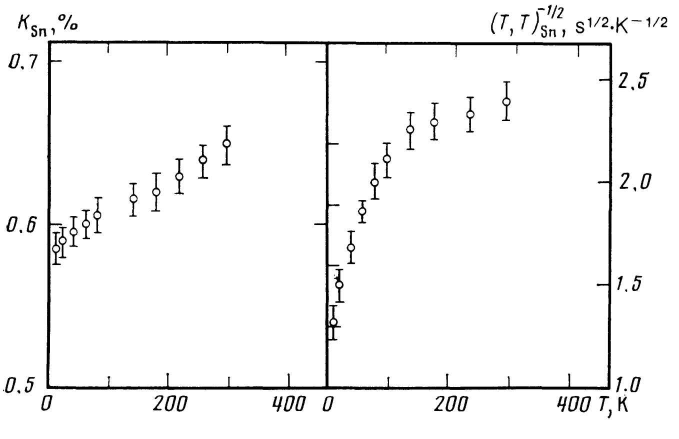

FIG. 3. Temperature dependences of the Knight shift K_{Sn} and of $(T_1T)^{-1}_{Sn}$ of the ^{119}Sn nuclei in SnMo$_6$Se$_8$.

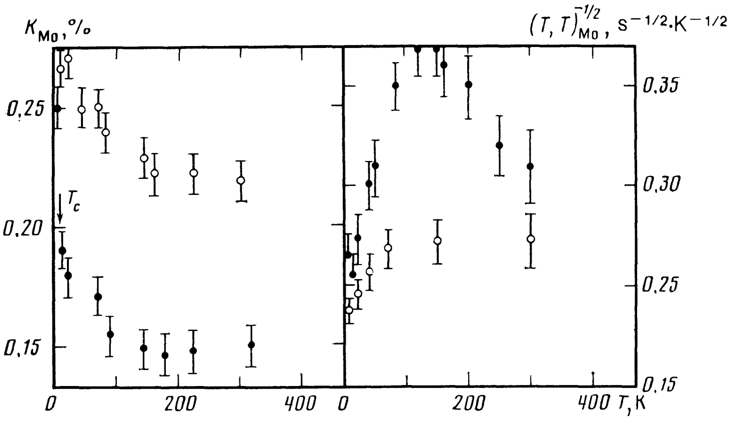

FIG. 4. Temperature dependences of the Knight shift K_{Mo} and of $(T_1T)^{-1/2}_{\mathrm{Mo}}$ of the ^{95}Mo nuclei in $SnMo_6Se_8$(○) and Mo_6Se_8(●).

of the magnetic susceptibility in these compounds, too. Indeed, below room temperature the different signs of the derivatives d_χ/dT and dK_{Mo}/dT indicate that the changes of the ^{95}Mo Knight shift are due to the contribution of the core polarization by d-electrons of the conduction band. The values $H_d(SnMo_6Se_8) = 1.25\cdot 10^5$ Oe and $H_d(Mo_6S_8) = -1.6\cdot 10^5$ Oe determined from the slope of $K(\chi)$ are close to the corresponding value for $SnMo_6Se_8(-1.6\cdot 10^5$ Oe). The proportionality of the values of K_{Mo} to $(T_1T)^{-1/2}$, with allowance for the measurement error, permit an estimate of the possible change of the Van Vleck contribution in this temperature range, viz., $\Delta\chi_{\mathrm{orb}} \leqslant 0.2\Delta\chi$.

The indicated correlations of the temperature dependences of χ, the Knight shift, and $(T_1T)^{-1/2}$ for the ^{119}Sn and ^{77}Se nuclei are probably due to the presence of hybridization of the molybdenum states with the states of tin and selenium near the Fermi level. A similar behavior was observed in Ref. 5 for ^{119}Sn in $SnMo_6S_8$, where sulfur replaces the chalcogen. The following expressions can be written for the Knight shifts and for the spin-lattice relaxation rates of ^{119}Sn and ^{77}Se:

$$K(\mathrm{Sn},\mathrm{Se}) = K_0 + \frac{1}{\mu_B} H_{\mathrm{polar}}\, \chi_d(T), \qquad (2)$$

$$(T_1T)^{-1}(\mathrm{Sn},\mathrm{Se}) = (T_1T)_s^{-1} + (T_1T)^{-1}_{\mathrm{polar}}, \qquad (3)$$

where K_0 and $(T_1T)_s^{-1}$ are contributions independent of temperature. The polarization contribution $(T_1T)^{-1}_{\mathrm{polar}}$ is proportional to the square of the Pauli susceptibility of the d-band electrons. In $SnMo_6S_8$ the polarization contributions were decisive in the behavior of the Knight shift and in the spin-lattice relaxation rate of the ^{119}Sn nuclei. The observed correlations of the Knight shfit $(T_1T)^{-1}$ of ^{77}Se and ^{119}Sn and of the magnetic susceptibility in $SnMo_6Se_8$ and Mo_6Se_8 are apparently also due to polarization contributions. This allows us to conclude that the decrease of the magnetic susceptibility of $SnMo_6Se_8$ and Mo_6Se_8 at $T > 300$ K is also due to a change of the Pauli contribution.

Thus, according to our data, the maximum of $\chi(T)$ in the compounds $SnMo_6Se_8$ and Mo_6Se_8 is related to the temperature dependence of the spin contribution of the d-band electrons. By the procedure used in Ref. 5 for joint analysis of the ^{95}Mo NMR data, we have separated the contributions made to the magnetic susceptibilities of these compounds for the purpose of estimating the spin contribution and the electronic density of states on the Fermi levels at various temperatures. It was assumed in the estimate that χ_{orb} is independent of temperature. The results of the separation are gathered in the table, which lists also the estimated corresponding contributions to the NMR characteristics of tin and selenium according to Eqs. (2) and (3). The obtained ratio of the contributions of the magnetic susceptibility is similar in many respect to the ratio obtained for $SnMo_6S_8$. The orbital contribution is almost completely compensated for by the diamagnetism of the ion core, and $\chi_s(SnMo_6Se_8)$ is smaller than the corresponding value in the ternary tin sulfide ($\chi_s(SnMo_6S_8) = 1\cdot 10^{-6}$ cm^3/mol). The maximum value of the Pauli contribution of the d-band electrons exceeds slightly the χ_d of the sulfide at room temperature. This result agrees with the band-calculation conclusion[1] that the densities of states of these compounds are close in the rhombohedral phase. The decrease of χ_d of the selenide and its increase in the sulfide with decrease of temperature lead to a spin-contribution ratio close to the ratio of the state-density estimates obtained from low-temperature estimates of the electron contribution to the specific heat. Thus, allowance for the temperature dependence of the Pauli contribution can explain the differences between the experimental and theoretical estimates of the density of states in $SnMo_6Se_8$. The value of χ_s of the binary compound is practically zero. An estimate of the density of states of Mo_6Se_8 without allowance for the exchange enhancement of the observed value of χ_d yields $N(0) = 1.5$ [eV·(Mo atom)·spin]$^{-1}$ for $T = 150$ K, larger by 1.5 times than the value obtained from band calculations.

The exchange enhancement of χ can be taken into account by analyzing the polarization contributions to the Knight shift and to the spin-lattice relaxation rate, which are proportional to χ_d for tin and selenium nuclei. As discussed in the preceding paper, it is possible to use for these contributions the Korringa relation, assuming that its deviation from the value $(K^2T_1T) = 2\mu_B{}^2/\gamma^2 hk_B$ for a free electron gas is due mainly to the presence of electron correlations. In units of $2\mu_B^2/\gamma^2 hk_B$ the Korringa product (K^2T_1T) for the corresponding polarization contribution amounts for $SnMo_6Se_8$ to $1.9-2.1$(^{77}Se) and $1.5-3.0$(^{119}Sn) and for Mo_6Se_8 to $1.9-2.6$(^{77}Se). The first value is for $T = 10$ K and the second for the temperature region in which χ is a maximum. Note the substantial discrepancy between these data and those given in Ref. 11 for $SnMo_6Se_8$. In the case of ^{119}Sn this is apparently due to the assumption made in Ref. 11 that the Knight shift for tin in the ternary compound $SnMo_6Se_8$ is entirely of spin origin. In the Fermi-liquid approximation,[12] the estimates obtained for the exchange integral are close to those obtained in Ref. 5 for $SnMo_6Se_8$ via., $J(SnMo_6Se_8) = 0.45(10)$ eV and $J(Mo_6Se_8) = 0.40(10)$ eV.

The table lists the values of the single-particle density of states $N(0) = \chi_d/(2\mu_B^2 + J_{\chi d})$ near the Fermi level for temperature close to T_c and for the region where χ is a maximum. The value of $N(0)$ obtained for $SnMo_6Se_8$ at $T \gtrsim T_c$ agrees well with the estimates of Ref. 3. The value listed in the table is smaller by approximately a factor 1.5 than that obtained by reducing the specific heat data of Ref. 3. It should be noted that the values of $N(0)$ obtained for the region of maximum χ agree satisfactorily with the results of band calculation for Mo_6Se_8 and $SnMo_6Se_8$ (Ref. 1). Moreover, analysis of the ^{95}Mo Knight-shift anisotropy and of the values of $(T_1T)^{-1}_{\rm Mo}$, similar to the analysis of Ref. 5, leads to the conclusion that the predominant role on the Fermi level is that of $4d$ states of molybdenum with orbital symmetry $d_{x^2-y^2}$ and d_{xy}; these states are degenerate in energy for the C_{4v} symmetry of the nearest surrounding of the Mo atoms: $N_{eg}(0)/N(0) > 0.6$ for the investigated compounds.

In conclusion, one more assumption can be advanced concerning the causes of the maximum on the $\chi(T)$ temperature dependences in the compounds Mo_6Se_8 and $SnMo_6Se_8$. One cannot exclude near the maximum temperature a possible distortion of the initial rhombohedral structure of these systems, and an associated restructuring of the electronic spectrum. A similar structure distortion takes place apparently in $SnMo_6S_8$ at lower temperatures. Such a distortion in the systems Mo_6Se_8 and $SnMo_6Se_8$ can cause the density of states on the Fermi level to decrease with decrease of temperature. Further investigations of the structure of the compounds investigated in the present study are needed to check on this assumption.

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