Low-temperature specific heat of $MoSi_2$

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We report specific-heat measurements on a single crystal of $MoSi_2$ between 0.2 and 7 K. ($\gamma=0.57$ mJ/mol K^2, $\Theta_D \simeq 500$ K.) The electronic contribution is in good agreement with other band-structure determinations. The lattice contribution is compared with sound-velocity measurements also reported and is discussed.

I. INTRODUCTION

$MoSi_2$ has been extensively studied because of its potential for applications in semiconductor devices. Single crystals of very high purity can be grown (residual resistivity ratio larger than 1000),[1] and many physical investigations have been carried out on this material.[2–7] We report here specific-heat measurements at very low temperatures, which we compare to the sound velocity, and which we discuss in relation to other results.

II. RESULTS AND ANALYSIS

The specific heat of a piece of a single crystal (1.285 g weight) has been measured between 0.2 and 7 K. The residual resistivity ratio measured on a sample from the same batch is $R(293\ \text{K})/R(4.2\ \text{K})=520$. We used a dilution refrigerator and a transient heat-pulse technique, the temperature varying step by step, as already described.[8] The sample was glued with epoxy resin to a silicon slice as support. The heat capacity of the other addenda was measured in separate experiments. However, uncertainty remains about the exact contribution of the heat capacity of the epoxy resin between 1.8 and 4 K, which makes difficult the analysis of the lattice contribution of $MoSi_2$ in this temperature range. Moreover, the large T^3 contribution of the addenda above 2.5 K, which then exceeds that of the sample, is at the origin of the scattering of the data. The specific heat of $MoSi_2$ is reported in Fig. 1. It can be analyzed in the usual way by a $\gamma T+\beta T^3$ law, sum of an electronic and lattice term, in the whole temperature range, although some deviation from a pure T^3 law (i.e., including terms of higher power) seems to appear above 5 K. These two contributions are also indicated in Fig. 1. The value of the γ coefficient is determined with an excellent accuracy, as seen either in Fig. 1, or by means of a C/T versus T^2 plot (Fig. 2), to be 3.75 ± 0.05 μJ/g K^2 or 0.57 ± 0.01 mJ/mol K^2, which corresponds to a density of states:

$$N(E_F)=3\gamma/\pi^2 k_B^2=0.24\ \text{states/eV unit-cell}\ .$$

For the determination of the lattice contribution C_l,

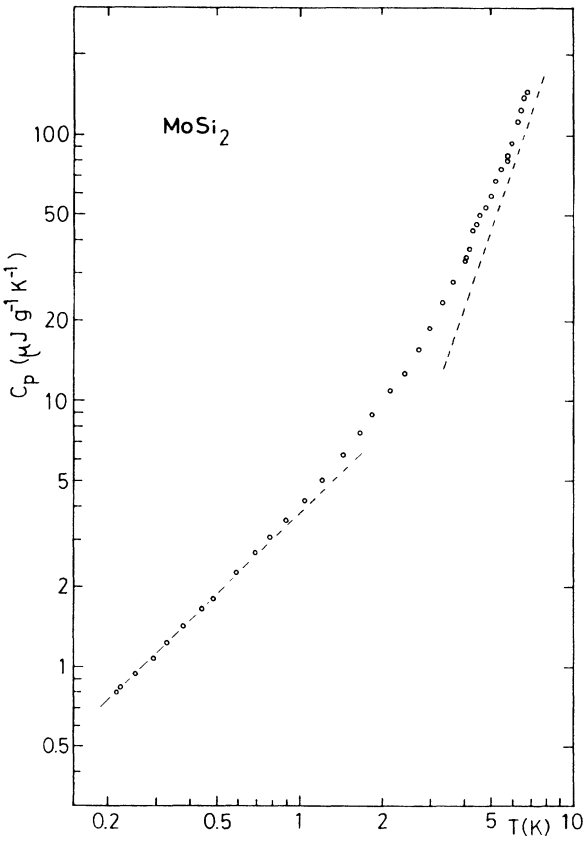

FIG. 1. Specific heat of $MoSi_2$ in a log$C$ vs log$T$ plot. Dashed lines represent the electronic contribution γT (below 1.8 K) and the mean βT^3 contribution above 3.5 K.

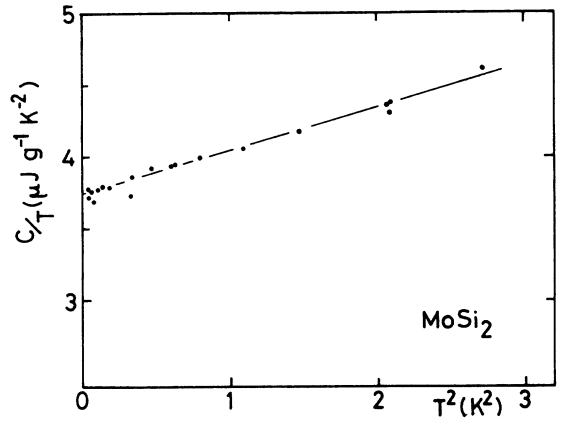

FIG. 2. C/T vs T^2 below 1.8 K.

we have considered two temperature ranges. Below 1.8 K, from the C/T versus T^2 diagram, we obtain $\beta=0.30\pm0.015$ μJ/g K^4 or 46 ± 2 μJ/mol K^4, corresponding to $\Theta_D=502\pm7$ K [$\beta=r\frac{12}{5}R(\pi^4/\Theta_D^3)$, with R the gas constant and $r=3$]. Above 4 K and up to 7 K, we have deduced the lattice contribution C_l after subtracting from C_p the electronic contribution γT, and analyzed it as $C_l/T^3=(C_p-\gamma T)/T^3$ (Fig. 3). Despite the scattering of the data, as explained previously due to the large amount of the addenda contribution, there is some indication for a progressive deviation at increasing T from the exact T^3 regime defined at the lowest temperatures. If one considers now Θ_D as a parameter dependent on T, it decreases from a value of about 500 K (defined below 1.8 K) to about 470 K around 7 K. To summarize, one can define over the whole temperature range of this experiment a value of Θ_D included between 470 and 510 K.

III. DISCUSSION

A. Electronic density of states

Band-structure calculations of $MoSi_2$ (Refs. 9 and 10) show that the Fermi level is located near a minimum of the density of states (DOS), at the intersection of an electronlike band and a holelike band. Both originate mainly from the d orbitals of molybdenum. $N(E_F)$ deduced from the specific-heat measurement is in quite good agreement with these calculations. See for instance the total DOS curve in Fig. 4 of Ref. 9. However, in this part of the curve, $N(E)$ varies very rapidly with E, and the resolution in E is not good enough to fix the value of the DOS at E_F with sufficient accuracy and this agreement could be viewed as fortuitous.

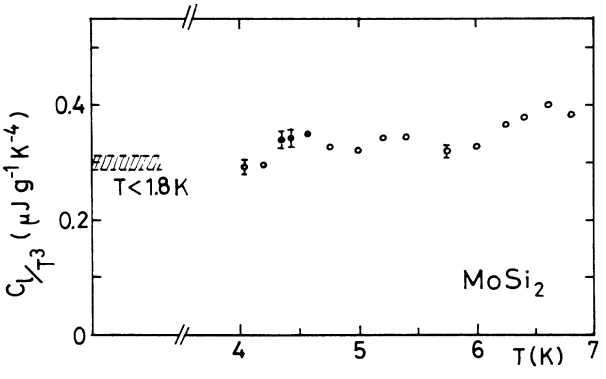

FIG. 3. Lattice contribution reported as C_l/T^3 against T. Dashed area corresponds to the β value determined below 1.8 K from the diagram C/T vs T^2 of Fig. 2.

Magnetoresistance measurements of $MoSi_2$ (Ref. 3) show that this compound is a compensated metal ($n_{h+}=n_{e-}$). Results are well accounted for by a carrier concentration of 0.04 electrons (or holes) per unit cell. Such a value, assuming free carriers, leads to $\gamma=0.78$ mJ/mol K^2 for the electronic coefficient of the specific heat which is about 30% larger than the measured value.

de Haas–van Alphen effect[4] which, contrary to the electrical conductivity and to the specific heat, is affected only by some parts of the Fermi surface, gives a smaller carrier concentration of 0.03 electrons (or holes) per unit cell for each band, which corresponds to $\gamma=0.71$ mJ/mol K^2, and especially shows that the effective masses are systematically smaller than for free electrons. All these results are in very good agreement with the density of states reported here.

The electronic coefficient γ measured by specific heat is usually renormalized by interaction effects. For electron-phonon interaction which is the only effect which could be expected here, the bare density of states is multiplied by $1+\lambda$. One can think that the λ parameter is small since in the series of the refractory metal disilicides, only one compound is found to be a superconductor, that is $CoSi_2$ (Ref. 11) and with a low critical temperature of about 1 K. Moreover we can make a rough estimate of λ from the ideal resistivity, which can be written as

$$\rho=\frac{2\pi m k_B}{n_p e^2\hbar}(n-1)\lambda_{\rm tr}\frac{T^n}{\Theta^{n-1}}J_n\left[\frac{\Theta}{T}\right],$$

with

$$J_n(x)=\int_0^x\frac{z^n dz}{(e^z-1)(1-e^{-z})},$$

where n_p is the carrier concentration, Θ is the Debye temperature, and $\lambda_{\rm tr}$ is comparable to the usual electron-phonon parameter.[12] The comparison of these expressions with the measurement reported in Ref. 3 leads in all cases to values for $\lambda_{\rm tr}$ smaller than 0.1 which shows that renormalization effects are negligible in the electronic specific heat of $MoSi_2$.

B. Lattice contribution

Preliminary ultrasound measurements of $MoSi_2$ were undertaken on the same sample. Longitudinal and shear acoustic modes were generated along the [100] and [001] directions. Complex echo patterns due to different acoustic modes were obtained in the two directions. Such observation yields that the sample could contain structural defects like mosaics or could be slightly misorientated.

As a consequence of mode coupling and interference it was difficult to measure with accuracy the velocity of the different acoustic modes associated with the tetragonal symmetry. Nevertheless, measurements gave about 7000 and 600 m/s for the velocity of the fastest longitudinal and the slowest shear modes, respectively.

A mean sound velocity $v_D = 4000$ m/s is calculated from the low-temperature specific-heat limit using

$$\frac{C}{T^3} = \frac{2\pi^2}{5} \frac{k_B^4}{\hbar^3} \frac{1}{\rho v_D^3} ,$$

where ρ is the density (6.25 g cm^{-3}). This value of v_D is included between the minimum and maximum velocities determined by ultrasound measurement, and the agreement is quite reasonable. A systematic study of the elastic constants of $MoSi_2$ is in progress.

A good fit of thermal expansion measurements[1] between 4.2 K and room temperature was obtained, assuming a Debye law for the lattice specific heat, with $\Theta = 473$ and 574 K for the a and c crystallographic parameters, respectively.[7] Θ values obtained in that range of temperature are in relatively good agreement with the Debye temperature measured below 10 K. However, large thermal variations of Θ are frequently observed in metallic alloys. They are easily understood by considering the departure of the phonon spectrum from the simple Debye law [see, for instance, results for the related compound Nb_3Al (Ref. 13)]. The small variation of β reported above, occurring already at 7 K, corresponds to an initial decrease of Θ by about 30 K from its value at $T = 0$. Such a variation is also usual[14] and will be followed by an increase at larger T, as the thermal expansion has shown.

Large deviations appear between Θ calculated by fitting the resistivity with a Bloch-Grüneisen law[3] and the Θ_D value reported here. They result in part from the different range of temperature investigated, and in a larger part from the failure of this simple model to account well for the interband scattering which occurs in $MoSi_2$. We note a better agreement between the Debye temperatures deduced from thermal expansion and from resistivity for $TaSi_2$ which, contrary to $MoSi_2$, is a single band metal.[7,15]

IV. CONCLUSION

Specific-heat measurements of $MoSi_2$ at very low temperature are in good agreement with previous electronic structure results. Two bands, one electronlike, and one holelike, cross the Fermi level, with a total density of states $N(E_F) = 0.24$ states/eV formula unit.

The electron-phonon enhancement is negligible. Lattice specific-heat contribution is in accordance with sound-velocity measurements. A thermal variation of the Debye temperature is found. Ideal resistivity, where interband scattering is important, has to be reanalyzed, accounting for these new results.

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