

Spin fluctuations in paramagnetic chromium determined from entropy considerations

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(Received 11 March 1993)

We have analyzed the entropy of paramagnetic bcc Cr from the Néel temperature $T_N = 311$ K to the melting temperature $T_f = 2136$ K. It is shown that the total experimental entropy cannot be accounted for solely by a sum of a vibrational part and a Sommerfeld-type electronic term from a nonmagnetic electronic structure. The total entropy is obtained through an elaborate assessment of available experimental data on various thermodynamic properties. The vibrational part is based on phonon data obtained in neutron scattering experiments by Trampenau, and accounts also for anharmonic effects. The Sommerfeld-type electronic part is obtained from electron band-structure calculations. Our analysis suggests a magnetic contribution that is related to spin fluctuations and that increases with temperature. We compare Cr with the other group-VI transition metals, Mo and W, using results from our previous works. Cr, Mo, and W show striking similarities, e.g., in their anharmonic phonon softening, when considered as a function of the reduced temperature T/T_f , where T_f is the melting temperature. Since phonons dominate the heat capacity, their C_p vs. T/T_f plots are very similar.

Many of the intriguing physical properties of Cr are now well understood.¹ However, the nature of the paramagnetic state is still controversial.^{2,3} One purpose of this paper is to search for effects of spin fluctuations, as they might be revealed in thermodynamic data, and to extract a magnetic contribution to the entropy of paramagnetic Cr. Another aim is to compare Cr with the two other group-VI transition metals, Mo and W. In a previous paper,⁴ we discussed Mo and W, and found striking similarities in various high-temperature thermodynamic properties when they were considered at the same reduced temperature T/T_f , where T_f is the melting temperature.⁵ It is interesting to investigate if these similarities hold for all three group-VI transition metals, in spite of the magnetism in Cr.

Following Hasegawa,⁶ we write

$$S_{\text{el}} = S_{\text{band}} + S_{\text{mag}}. \quad (1)$$

$S_{\text{el}}(T)$ is the total entropy related to electronic excitations, S_{band} is the Sommerfeld-type entropy obtained from the electron density-of-states and S_{mag} is a hypothetical contribution from magnetic fluctuations. Then

$$S_{\text{mag}} = S_{\text{tot}} - S_{\text{ph}} - S_{\text{band}}, \quad (2)$$

where S_{tot} is the total experimental entropy and S_{ph} is the vibrational part. White, Roberts, and Fawcett^{7,8} noted that the right-hand side of Eq. (2) seems to be positive for Cr, thus suggesting a magnetic contribution. However, they based part of their discussion on the assumption that anharmonicity has a negligible influence on the heat capacity at constant volume. We have analyzed⁴ the high-temperature thermodynamic properties of Mo and W, and found a considerable anharmonic contribution also at fixed crystal volume. Hence, in order to detect a possible magnetic entropy, one must accurately account for S_{ph} . In our study, the phonon part is

taken from experiments by Trampenau,⁹ who measured the phonon dispersion curves for Cr up to 1773 K using neutron scattering. Further, S_{tot} is obtained by us from an elaborate assessment of thermodynamic data, and S_{band} is taken from an electron band-structure calculation. Thus S_{mag} can be evaluated from Eq. (2). We remark that one of us¹⁰ has used an analogous approach to study spin fluctuations in fcc Fe at 1428 K.

The total entropy, $S_{\text{tot}}(T)$, of bcc Cr was evaluated from measured thermodynamic quantities as follows. Experimental data on the heat capacity, enthalpy, and standard entropy,¹¹⁻²⁰ lattice parameters and the coefficient of linear thermal expansion α ,²¹⁻²⁷ the isentropic bulk modulus B_S ²⁸⁻³² and the pressure derivative of B_S ³³ were all treated simultaneously, using a computer optimization technique³⁴ to get the molar Gibbs energy function $G_m(T, P)$ and quantities derived from G_m . The computer program, described in Ref. 34, minimizes the square sum of the differences between experimental and calculated values, while giving each piece of information a certain weight. These weights are selected by personal judgement, and changed by trial and error during the work, until the input data are accounted for within the expected uncertainty limits. This approach is now well established,³⁵ and it has been used by us, e.g., to study the thermodynamics of Mo and W.⁴ We believe that our $S_{\text{tot}}(T)$ is accurate to about 1%, and it also agrees well with previous independent evaluations.^{11,36,37} It should be remarked that, since we only want results referring to ambient pressure, the pressure dependence of G_m (i.e., the molar volume and related quantities), is not needed. However, our experience shows that including information on α and B_S in the assessment leads to an improved evaluation of G_m . For instance, the Grüneisen function, $\gamma_G(T)$, was found to be almost constant between $0.25T_f$ and T_f (cf. Fig. 1). Such a regular behavior of γ_G has been noted by us⁴ and by White⁸ to be a sign of internal consistency in thermodynamic data.

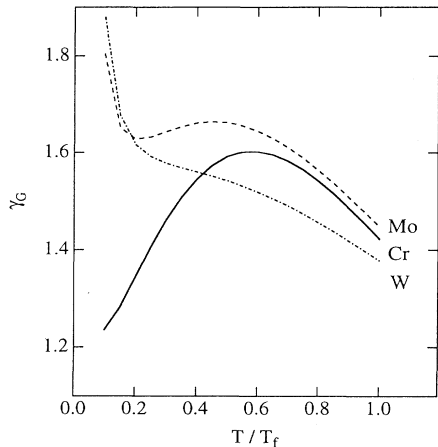


FIG. 1. The thermodynamic Grüneisen function $\gamma_G(T)$ vs the reduced temperature T/T_f , for Cr, Mo, and W.

For S_{ph} we rely on neutron scattering data by Trampenau.⁹ He reported phonon dispersion curves of Cr at 293 K, 673 K, 1073 K, 1473 K, and 1773 K, and the results were fitted to a Born–von Kármán model with interactions to the fifth neighbor. Trampenau then derived the phonon density-of-states at the temperatures cited above, and used it in the entropy expression for harmonic phonons to evaluate the vibrational entropy. We shall now argue that this $S_{\text{ph}}(T)$ is adequate for our analysis. It is known³⁸ that, to low order in perturbation theory, the anharmonic effects in $S_{\text{ph}}(T)$ are correctly accounted for if the phonon spectrum determined by neutron scattering is inserted into the entropy expression for harmonic vibrations. We note that the phonon resonances in the neutron scattering experiments are quite narrow and symmetrical, even at 1773 K,⁹ suggesting that the corresponding phonon frequencies can be directly used to calculate the entropy. However, our work⁴ on Mo and W and on other systems^{39,40} shows that higher-order anharmonicity is important at high temper-

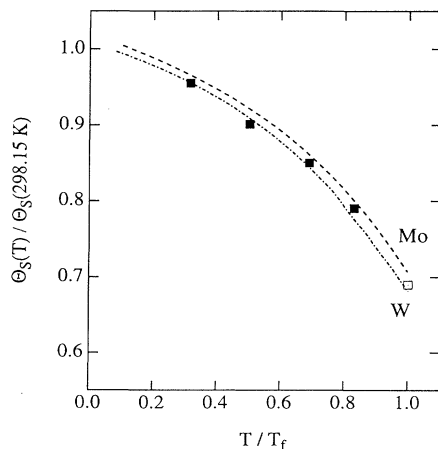


FIG. 2. The entropy Debye temperature Θ_S , normalized as $\Theta_S(T)/\Theta_S(298.15 \text{ K})$, and plotted vs the reduced temperature T/T_f . The curves for Mo and W are from our previous work.⁴ The filled squares refer to Θ_S values deduced from neutron scattering work by Trampenau (Ref. 9). The open square is our estimate.

atures. This is shown in Fig. 2, where we plot the entropy Debye temperature⁴¹ Θ_S , vs T/T_f , for Cr, Mo, and W. For harmonic lattice vibrations, Θ_S is constant at high temperatures, and with anharmonicity described by low-order perturbation theory, it decreases linearly in T . Θ_S for Mo and W in Fig. 2 are from our previous work,⁴ and the values for Cr (filled squares) are derived from the work by Trampenau. He reported results also for $T=293 \text{ K}$, i.e., below T_N . However, there are pronounced anomalies in some elastic constants around T_N , and one cannot exclude that Θ_S is significantly affected in that temperature region. The very small experimental entropy change at T_N , $35 \text{ mJ}/(\text{mol}\cdot\text{K})$,¹ might then be explained by a redistribution of entropy between vibrational and nonvibrational excitations when passing through T_N . We therefore prefer the following procedure to get $\Theta_S(298.15 \text{ K})$. Θ_S from Trampenau at 673 K, 1073 K, and 1473 K were plotted versus the thermal energy U .⁴² This gave a straight line which was extrapolated to 298.15 K, thus yielding $\Theta_S(298.15 \text{ K})=486 \text{ K}$ as our adopted value for the paramagnetic state.

Since Cr, Mo, and W belong to the same group in the Periodic Table, we expect them to behave similarly. Figure 2 confirms this idea for Θ_S . This also lends further support to the accuracy of the data of Trampenau.⁹ At $T = T_f$ we obtain S_{ph} through an extrapolation in Fig. 1 to get $\Theta_S=335 \text{ K}$ for Cr. We believe that our calculated S_{ph} for Cr is accurate to better than 0.5%, i.e., approximately corresponding to an error of 1.5% in Θ_S .

The Sommerfeld-type contribution to the electronic entropy, S_{band} , is given by

$$S_{\text{band}} = -k_B \int [f \ln f + (1 - f) \ln(1 - f)] N(E) dE, \quad (3)$$

where $N(E)$ is the electron density-of-states and f is the Fermi-Dirac function. Since we are interested in temperatures larger than a characteristic Debye temperature, there should be no electron-phonon many-body enhancement factor $1 + \lambda$.³⁸ We have calculated $N(E)$ using the linear muffin-tin orbital (LMTO) method⁴³ for nonmagnetic bcc Cr and for an antiferromagnetic state with two atoms per unit cell, using experimental lattice parameters. Our $N(E)$ are in excellent agreement with previous works.⁴⁴ At low temperatures, the entropies S_{band} derived from Eq. (3) for the nonmagnetic and the antiferromagnetic cases differ somewhat, but in the temperature range from T_N to T_f they agree to within 5%. With a constant $N(E)$, equal to the value at the 0 K Fermi level, S_{band} would increase linearly in T (dashed line in Fig. 3). The full line for S_{band} is obtained from Eq. (3), with $N(E)$ calculated for a lattice parameter that varies with T according to experiments. This is the electronic entropy to be used in our subsequent discussion. Of the difference between the full-drawn and dashed curves at $T = T_f$, about 1/3 is due to the varying $N(E)$ with thermal expansion, and 2/3 comes from the fact that $N(E)$ in Eq. (3) is not constant around the Fermi level. The finite lifetime of electrons will cause a broadening of electron states that affects $N(E)$.³⁸ We estimate that broadening effects could add $0.03R$ to S_{band} at $T = T_f$, but since this term is both small and uncertain, it is neglected in

the following discussion.

Figure 3 shows the entropy S_{mag} (per mole) calculated from Eq. (2) and with S_{tot} , S_{ph} , and S_{band} obtained as described above. The figure also gives $S_{\text{tot}} - S_{\text{ph}}$ and S_{band} . Figure 3 demonstrates that there is a substantial entropy in the paramagnetic state of Cr that cannot be accounted for by vibrational and Sommerfeld-type electronic excitations. We tentatively associate this term with magnetic excitations. Its presence should affect $N(E)$, and hence require a recalculation of the Sommerfeld-type entropy S_{band} . Since the nature of the spin fluctuations in Cr far above T_N is poorly known, it is not clear how such a recalculation should be carried out. We therefore try to get some insight by studying S_{mag} .

At the melting temperature of Cr, $S_{\text{mag}} = 0.42(\pm 0.08)R$ per mole, where R is the gas constant. We have then allowed for the maximum uncertainties discussed above. We note that this value agrees approximately with the entropy $S_{\text{mag}} = R \ln(2S + 1) = 0.48R$ that would result from a classical description of uncorrelated spins of magnitude $2S = n_B$, where the Bohr magneton number $n_B = 0.62$ is that of the antiferromagnetic ground state.¹ However, such a picture is too simplified. It would lead to an S_{mag} that saturates at $R \ln(2S + 1)$, while Fig. 3 suggests a magnetic entropy that continues to increase. At high temperatures we expect complicated magnetic excitations that involve both transverse and longitudinal fluctuations of the magnetic moments.⁴⁵ In addition, thermal expansion has an indirect effect on the magnetic state. From calculations⁴⁶ of dn_B/dV we conclude that the ground state of Cr would have $n_B = 1.3(\pm 0.2)$ if the lattice is expanded to the atomic volume at $T = T_f$.

Figure 2 showed some remarkable similarities in the anharmonic softening of Θ_S for Cr, Mo, and W, when plotted vs the reduced temperature T/T_f . The Grüneisen parameters of Cr, Mo, and W, given in Fig. 1, are also quite similar. In a previous paper,⁴ we considered the total heat capacity at constant pressure, C_p , and found that the values for Mo and W above room temperature agree to better than 1% when plotted vs T/T_f . Figure 4 gives those C_p for Mo and W, together with results for

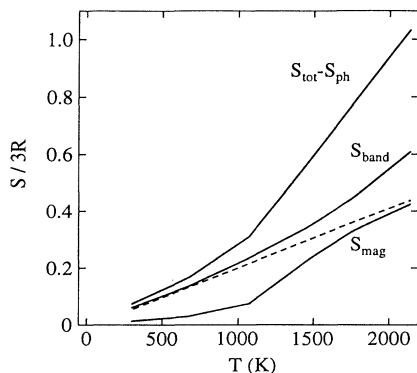


FIG. 3. The difference between the total and the vibrational entropy, $S_{\text{tot}} - S_{\text{ph}}$, the Sommerfeld-type electronic entropy, S_{band} , and the difference $S_{\text{mag}} = S_{\text{tot}} - S_{\text{ph}} - S_{\text{band}}$. The dashed line is a linear extrapolation of S_{band} from low temperatures.

Cr from the present work. The figure also shows a tentative magnetic contribution C_{mag} for Cr, obtained as $C_{\text{mag}} = T(dS_{\text{mag}}/dT)_p$, where S_{mag} is given in Fig. 3. It is seen that C_{mag} accounts for most of the difference between C_p of Cr and of Mo and W. The separation of the C_p curves at the low-temperature end is mainly due to differences in the Debye temperatures of Cr, Mo, and W.

In conclusion, we have studied the entropy of chromium, from the Néel temperature $T_N = 311$ K to the melting temperature $T_f = 2136$ K. The total entropy was obtained through an elaborate assessment of experimental data on various thermodynamic properties. The vibrational part was based on results from neutron scattering experiments by Trampenau.⁹ It includes substantial anharmonic effects. We find that the total entropy cannot be accounted for solely as a sum of a vibrational part and a Sommerfeld-type electronic term. The remaining entropy is tentatively ascribed to spin fluctuations. The disorder of the Cr ground-state magnetic moments is not sufficient to account for that entropy, thus suggesting that the moments increase in size with temperature. Our study considerably extends the temperature range above T_N , for which spin fluctuations in Cr have been discussed on the basis of experiments.

Relying on our previous work⁴ on Mo and W, we have also compared some thermal properties of the group-VI transition metals (Cr, Mo, and W). There are remarkable similarities between Mo and W that we have found to extend also to Cr, in spite of its magnetic structure. In particular, the anharmonic softening of the entropy Debye temperature Θ_S closely agrees for Cr, Mo, and W when plotted vs T/T_f . Since the phonon part dominates the total heat capacity, C_p vs T/T_f for Cr is similar to that of Mo and W.

We gratefully acknowledge discussions with J. Trampenau, W. Petry, P. Fulde, and L. Falicov. This work was supported by the Swedish Natural Science Research Council, The Swedish National Board for Industrial and Technical Development, The Swedish Research Council for Engineering Sciences, and the Göran Gustafsson Foundation.

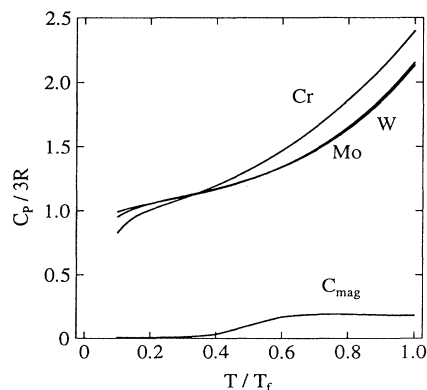


FIG. 4. The total heat capacity C_p , plotted vs the reduced temperature T/T_f , for Mo and W⁴ and for Cr (this work). Also shown is a tentative magnetic heat capacity, $C_{\text{mag}} = T(dS_{\text{mag}}/dT)_p$, where S_{mag} is given in Fig. 3.

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