Spin disorder in paramagnetic fcc iron

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From available information on the total entropy of fcc iron, its phonon density of states at 1428 K, and its electron density of states, the entropy due to disorder of the persistent spins in the paramagnetic state at 1428 K is estimated as $S_{mag}/R = 0.8 \pm 0.1$. This should be compared with the entropy of completely disordered spins of magnitude S_a per atom, which would be $S_{mag}/R = \ln(2S_a+1) = 1.2$, if we take $2S_a = 2.4$ from band-structure calculations. This comparison indicates that there is very little correlation between the directions of the average magnetic moments at neighboring lattice sites.

I. INTRODUCTION

It is well established[1] that bcc and fcc iron have persistent magnetic moments in the paramagnetic state at high temperatures, but not much is known about their short-range order.[2] For bcc iron, one can estimate the associated spin-disorder entropy from the measured heat capacity around the Curie temperature, if a smooth nonmagnetic background is subtracted.[3,4] The fcc lattice of pure iron is stable only between 1183 and 1675 K. There the heat capacity is featureless, and gives no information about the magnetic entropy. However, the phonon-frequency spectrum of fcc iron at 1428 K has recently been measured by Zarestky and Stassis.[5] They also deduced the phonon density of states $F(\omega)$. The present report uses that result, together with experimental data on the total entropy and results from band-structure calculations, to get a quantitative estimate of the spin disorder in the paramagnetic states of fcc iron.

II. ENTROPY CONTRIBUTIONS

A. Lattice vibrations

The vibrational entropy at temperature T, with anharmonic corrections included to low order in perturbation theory,[6] is given by the harmonic expression but with the phonon frequencies referring to T. The leading terms in the high-temperature expansion of the vibrational entropy are (per mole, R is the gas constant)

$$S_{vib} = 3R[\tfrac{4}{3} + \ln(T/\Theta) + \tfrac{1}{40}(\Theta/T)^2 + \cdots]. \quad (1)$$

Here $\Theta = \Theta(0)$ is a high-temperature-entropy Debye temperature. This is a special case of the Debye temperatures $\Theta(n)$ which are derived from the nth moment of the phonon frequencies for harmonic vibrations. See, e.g., Rosén and Grimvall[7] or Grimvall[8] for details on the vibrational entropy. From the precise form of $F(\omega)$ (Ref. 9), I calculate $\Theta(0) = 329$ K. The variation of $\Theta(n)$ with n is unusually weak in fcc iron. Zarestky and Stassis[5] give $\Theta(-3) = 324$ K and from their graph one reads $\Theta(2) = 334$ K. With $\Theta(0) = 329$ K, Eq. (1) yields $S_{vib} = 69.89$ J/mol K at 1428 K. The uncertainty is only 0.24 J/mol K if $\Theta(0)$ is uncertain by 1%.

B. Spin disorder

Let S_{mag} be the entropy associated with the spin disorder. In a model with completely disordered localized atomic spins of magnitude S_a, one has

$$S_{mag}/R = \ln(2S_a+1). \quad (2)$$

Heine and Joynt[2] discussed the entropy of a block of spins, with an average tilt angle ϕ between nearest-neighbor spins. Their expression for the spin-disorder entropy S_{HJ} is ($t = 2\phi/\pi$)

$$S_{HJ}/R = t^3 \ln(2S_a t^{-3}+1). \quad (3)$$

With complete spin disorder ($\phi = \pi/2$, $t = 1$) we recover Eq. (2).

Kübler[10] calculated the magnetic moments in the ferromagnetic and antiferromagnetic phases of fcc iron as a function of the lattice parameter (Wigner-Seitz radius r_S, in a.u.). The ferromagnetic moment varies strongly with r_S, from a low-volume value around $2S_a = 0.7$ to a high-volume value around 2.3. The antiferromagnetic moment lies between these values. The observed atomic volume at 1428 K corresponds to the high moment in Kübler's work. Wang, Klein, and Krakauer[11] obtained $2S_a = 2.47$ in the high-moment ferromagnetic state and $2S_a = 0.64$ in the antiferromagnetic state. Bagayoko and Callaway[12] obtained a moment for ferromagnetic fcc iron which varies rapidly with r_S, and is about $2S_a = 2.5$ at the observed atomic volume. They also found smaller moments in the ferromagnetic low-volume state and in the antiferromagnetic state. These values can be compared with $2S_a = 0.9$, obtained by Brown *et al.*[1] from diffuse neutron scattering in fcc iron at 1320 K. However, the latter value is an average which does not resolve fluctuations over times shorter than 10^{-13} s and it should not be used in a discussion of disorder entropy. Hasegawa and Pettifor[13] obtained a local magnetic moment in the fcc phase which is almost independent of T above 1000 K and of the approximate magnitude $2S_a = 2.1$. Lacking precise information

about the moment in the paramagnetic state, I will rely on the results for the magnetically ordered states and take $2S_a = 2.4$ in the subsequent discussion.

C. Electronic excitations

In the simplest model, the electronic entropy due to single-particle excitations is $S_{el} = \gamma T = (\pi^2/3) k_B^2 N(\mu_F) T$, where $N(\mu_F)$ is the electron density of states at the Fermi level (both spin directions). Since we are interested in the high-temperature behavior there is no electron-phonon enhancement factor. However, it is not clear what $N(\mu_F)$ one should use in a paramagnetic state with persistent and disordered spins. Theoretical calculations refer either to a completely nonmagnetic state or to a uniformly spin-polarized state, but $N(\mu_F)$ turns out not to be very different in these two cases. Calculations for the ferromagnetic state by Bagayoko and Callaway[12] and by Kübler[10] and for the nonmagnetic state by Kübler (after interpolation or extrapolation to the observed atomic volume of fcc iron at 1428 K, i.e., $r_S = 2.71$) fall in the interval $S_{el}/R = 0.74 \pm 0.1$ at 1428 K. One may note that S_{el} probes the electron density of states $N(E)$ in a "window" of the approximate width $3k_BT$ around the chemical potential μ_F. In view of the uncertainty in $N(E)$, such effects are neglected.

III. ANALYSIS AND CONCLUSIONS

A recent assessment[14] of the experimentally determined thermal functions of iron gives, for the total entropy at 1428 K, $S_{tot} = 82.54$ J/mol K. This is very close to the value 82.47 J/mol K recommended by Hultgren *et al.*[15] Then, $S_{mag} + S_{el} = S_{tot} - S_{vib} = (82.54 - 69.89)$ J/mol K $= 12.65$ J/mol K, or

$$S_{mag}/R = 1.52 - S_{el}/R . \quad (4)$$

With $S_{el}/R = 0.74$ (Sec. II C) one has $S_{mag}/R \approx 0.8 \pm 0.1$, with the uncertainty estimated here. There seems to be only one previous estimate of S_{mag} for the fcc paramagnetic state. Grimvall,[16] in different fits to thermodynamic data and to the temperature-pressure phase diagram of iron, obtained $S_{mag}/R \approx 0.8$ and 0.9, respectively, but those estimates may have nonmagnetic corrections.[4] One may also compare with Hasegawa and Pettifor[13] who obtained $(S_{mag} + S_{el})/R = 0.94$ (estimated here from their $-\partial F/\partial T$) in a theoretical electron-band-structure calculation. The present result, which is derived from experiments at 1428 K, should be the most reliable.

There has been a considerable controversy about the short-range order in the paramagnetic states of iron, expressed, e.g., as the average tilt angle ϕ between the magnetic moments on neighboring lattice sites.[2] Equation (2), with $2S_a = 2.4$ (Sec. II B), yields $S_{mag}/R = 1.22$ for completely disordered moments. This is not much larger than the present estimate $S_{mag}/R = 0.8$ from Eq. (4), which indicates that there is little short-range order in paramagnetic fcc iron. Equation (3), with $2S_a = 2.4$, would give the average tilt angle $\phi \approx 67°$. This should be compared with $\phi \approx 60°$ obtained by Heine and Joynt[2] in their analysis of paramagnetic bcc iron.

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