Explanation for the Configurational Heat Capacity of Ordered Phases

Sluiter Marcel, Kawazoe Yoshiyuki

Journal or publication title: Physical Review. B
Volume: 59
Number: 5
Page range: 3280-3282
Year: 1999
URL: http://hdl.handle.net/10097/53209
doi: 10.1103/PhysRevB.59.3280
Explanation for the configurational heat capacity of ordered phases

Marcel Sluiter and Yoshiyuki Kawazoe
Institute for Materials Research, Tohoku University, 980-8577 Sendai, Japan
(Received 11 September 1998)

Recently, an intriguing “W shape” has been reported for the curve of the configurational heat capacity versus composition. This feature is calculated in ordered phases with various methods. A detailed explanation has not been published, so a brief derivation and explanation of its origin is in order. Within the context of a Bragg-Williams model expressions for the heat capacity are derived. These expressions indicate that the W shape originates from the composition dependence of the order parameter.

\[ C_v = \left. \frac{\partial U}{\partial \eta} \right|_{c,v} \left( T \frac{\partial^2 F}{\partial \eta^2} \right). \]  

Equation (4) allows one to compute analytically the heat capacity at a fixed composition with, e.g., the cluster variation method. Hence, finite difference calculations with limited accuracy are not necessary.

In order to explain the composition dependence of \( C_v \), the \( \partial U/\partial \eta \) and \( \partial^2 F/\partial \eta^2 \) are now examined. Quite generally, the internal energy can, to a good approximation, be written as a sum over pairwise interatomic interaction terms

\[ U = - \sum_{a,b,i,j} W_{i,j}^{a,b} c_i^a c_j^b, \]

where \( W_{i,j}^{a,b} \) refers to the (positive) interaction between atomic species \( i \) and \( j \) on sublattices \( \alpha \) and \( \beta \), and where \( c_i^a \) is the \( \alpha \) sublattice concentration of the \( i \) species.

The concentration of the \( i \) species \( c_i \) is a sum over the sublattice concentrations, whereas the order parameter is a difference of sublattice concentrations. Therefore, \( U \) generally has a quadratic and \( \partial U/\partial \eta \) has a linear dependence on \( \eta \). From now on, for brevity, cases with two species only will be considered, so that the composition can be uniquely specified with a single parameter \( c = c_1 \), however, the treatment is equally valid for cases with larger numbers of species.

FIG. 1. Heat capacity \( C_v \) in units of \( k_B \) as a function of composition \( c \). Parameters: \( W = 20 \), \( k_B T = 1.5 \), see text.
The maximal attainable value of the order parameter \( \eta_{\text{max}} \) can be determined from minimizing the internal energy only. After all, the internal energy is the driving force for ordering, whereas the entropy destroys the ordering. The internal energy must be minimized with respect to the constraints of the composition being at a particular value, and of the sublattice concentrations remaining within the interval \([0,1]\). As the internal energy and the constraints are all linear in the sublattice concentrations, \( \eta_{\text{max}} \) at some particular composition is a linear function of the composition. In fact, \( \eta_{\text{max}} \) is a piecewise linear function as can be shown for the case of an order parameter normalized to unity with two atomic species and two sublattices

\[
\eta_{\text{max}} = c/c^{\text{stoi}} \quad \forall c \leq c^{\text{stoi}},
\]

\[
= (1 - c)/(1 - c^{\text{stoi}}) \quad \forall c \geq c^{\text{stoi}},
\]

where \( c^{\text{stoi}} \) is the stoichiometric composition. At low temperature, \( \eta \) will tend toward \( \eta_{\text{max}}, \) see Fig. 2. In Fig. 2 results for the B2 (cesium chloride type) ordered phase, as computed in the Bragg-Williams approximation, are shown. As was discussed above, \( \partial U/\partial \eta \) is proportional to \( \eta, \) so that, at not too high a temperature, the composition dependence of \( (\partial U/\partial \eta)^2 \) can be approximated by that of \( \eta_{\text{max}}^2. \) While this curve does produce a maximum at stoichiometry, it is too wide to explain the sharp narrow peak that occurs in \( C_v(c). \)

Actual calculations bear this out, see Fig. 3, as for the case of a B2 ordered structure for which the internal energy is given by

\[
U = -\frac{1}{2} W(c - c^2 + \eta^2),
\]

where \( \eta = |c^a_i - c^b_i|/2 \) (normalized to 1/2), and \( W = 20. \) In the Bragg-Williams approximation the order-disorder temperature \( T_0 \) is given by \( k_B T_0 = W/8. \)

The narrow peak in \( C_v(c) \) at stoichiometry, therefore, must derive from \( \partial^2 F/\partial \eta^2. \) This term can be split in two parts, second derivatives of the internal energy and entropy, respectively. Above it was shown that the internal energy is proportional to \( \eta^2, \) so that its second derivative cannot produce the sharp peak in \( C_v. \) Hence, \( \partial^2 S/\partial \eta^2, \) only, remains.

As a first order approximation of the entropy, the single site entropy must derive from \( U \) at not too high a temperature, the composition dependence of \( \eta^2, \) so that, \( \eta^2 \) has a rather sharp maximum at stoichiometry than at other compositions just slightly away from stoichiometry, see Fig. 2. The larger difference of \( \eta_{\text{max}} - \eta \)

![FIG. 2. Maximum order parameter \( \eta_{\text{max}} \) (thick solid line), and actual order parameter \( \eta \) (dashed line), as a function of composition \( c. \) Parameters as in Fig. 1.](image)

![FIG. 3. Square of the derivative of the internal energy \( U \) with respect to the order parameter \( \eta \) as a function of composition \( c. \) Parameters as in Fig. 1.](image)
The sharp peak in $C_v$ thus, is explained in terms of sublattice concentrations. At finite temperature, at stoichiometry, a certain number of antisite defects exist. In a binary alloy of $A$ and $B$ atoms there are then equal numbers of $A$ atoms on the $\beta$ sublattice as $B$ atoms on the $\alpha$ sublattice. When some $A$ atoms are replaced by $B$ atoms, to make the alloy off-stoichiometric, the number of $B$ atoms on the $\alpha$ sublattice becomes bigger, but the number of $A$ atoms on the $\beta$ sublattice becomes smaller. Hence, introducing off-stoichiometric defects has made the smallest sublattice concentration smaller so that the entropy term becomes more negative, see Fig. 4. This effect is the main cause of the sharply peaked $C_v(c)$ curve.

When the temperature is lowered, the order parameter increases, and the smallest sublattice concentrations approach zero more closely. Therefore, at low temperatures the peak at stoichiometry in the $C_v$ curve becomes more pronounced.

Far from stoichiometry $C_v$ increases, see Fig. 1. This too, is readily apparent from the large difference $\eta_{\text{max}} - \eta$ seen in Fig. 2, and from Eq. (7). Far from stoichiometry the order breaks down because the internal energy term becomes small compared to the entropy term. Hence, both right at, and far from stoichiometry $\eta$ differs much more from $\eta_{\text{max}}$ than is the case just a little away from stoichiometry, see Fig. 2. Therefore, $C_v$ takes large values both at, and very far from stoichiometry.

A Bragg-Williams model has been used to explain the W shape of the configurational heat capacity versus the composition for ordered phases. It was shown that the heat capacity at low temperature with nearly optimal ordering is proportional to the difference of the maximal attainable order parameter and the actual order parameter. The maximal attainable order parameter has a singularity at stoichiometry, unlike the actual order parameter at nonzero temperature, so that the difference of the maximal attainable and actual order parameters has a peak at stoichiometry. At the compositional limit of the ordered state, the order breaks down and the actual order parameter differs much from the maximal attainable value, causing again an increase in the heat capacity. In terms of the sublattice concentrations it was explained that near stoichiometry, the heat capacity is proportional to the smallest sublattice concentration. When off-stoichiometric defects are introduced, on at least one sublattice, the concentration of antisite defects becomes very small, causing a minimum in the heat capacity just away from stoichiometry, as a consequence, at stoichiometry a maximum occurs.

Although, these results have been derived using a Bragg-Williams description, the relations between the various properties should be qualitatively model independent. As such, the peak in the heat capacity, and its origin, should be generally valid.

M.S. wishes to thank Professor Sundman for bringing this topic to his attention.

---
