Thermal Expansion Study of Ordered and Disordered Fe$_3$Al: An Effective Approach for the Determination of Vibrational Entropy

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Thermal expansion measurements have been performed on chemically disordered and $D0_3$ ordered Fe$_3$Al alloy using the capacitance dilatometric method. A semiclassical model has been used to obtain the anharmonicity parameters and accurate values of the Debye and Einstein temperatures. An estimate of the vibrational entropy difference between the ordered and disordered phases of the alloy is also obtained using this approach.

Considerable effort has lately gone into understanding the role of lattice vibrations in the thermodynamics of chemical ordering in binary substitutional alloys [1–8]. It has been suggested [6,7] in this connection that the contribution of vibrational entropy to the phase stability in alloys can be quite significant. Historically, Nix and Shockley [9] first suggested that the state of order could affect the lattice vibrations through a change in Debye temperature. They showed that the vibrational entropy difference (ΔS_{vib}) between an ordered and disordered phase of an alloy would be given by

$$\Delta S_{vib} = S_{vib}^D - S_{vib}^O = 3R \ln\left(\frac{\Theta^O}{\Theta^D}\right), \qquad (1)$$

where Θ is the Debye temperature and the superscripts O and D refer to the ordered and disordered phases, respectively. Surprisingly enough, the vibrational entropy contribution has remained largely neglected as compared to the configurational entropy for quite some time. Later, several theoretical calculations [10–15] followed, emphasizing its significance. For example, it has been shown that the incorporation of vibrational entropy term in the free energy can lead to a sizable reduction in the critical temperature for ordering [10–12,15]. Experimentally, however, no direct evidence for the importance of vibrational entropy was available until recently when Anthony, Okamoto, and Fultz [6] measured the difference in vibrational entropy between $L1_2$ ordered Ni$_3$Al and its disordered fcc solid solution. They estimated ΔS_{vib} to be about 0.3 k_B/atom which is a substantially large contribution as compared to the configurational entropy of mixing (0.56 k_B/atom). Subsequently in a follow-up work [7], the vibrational entropy difference between disordered (bcc) and $D0_3$ ordered Fe$_3$Al was also measured by them directly by calorimetric studies, and ΔS_{vib} was found to be 0.1 k_B/atom. In the present communication we suggest that thermal expansion measurements can be used as yet another direct and useful method of studying the difference in the lattice vibrational behavior of an ordered and a disordered alloy. We have employed this method to determine the Debye temperatures and vibrational entropies of disordered and $D0_3$ ordered Fe$_3$Al alloys and

have thus obtained an estimate of the vibrational entropy difference (ΔS_{vib}) between these two phases.

Accurate thermal expansion measurements in the temperature range 80–300 K were carried out using a simple but versatile three-terminal capacitance dilatometer. The schematic cell design is shown in Fig. 1. It consists of two capacitor plates (C_1 and C_2) made out of copper. C_1 is rigidly fixed to the base (B), whereas C_2 is free to move and pressed against the sample (S) by three phosphor bronze springs (S_1, S_2, S_3). The other ends of these springs are also rigidly attached to the base (B). A copper chamber (C) encloses the plates and the sample, and serves as the third terminal (ground) of the capacitance cell. Sample temperature is maintained and controlled by a Lakeshore model DRC91C temperature controller using a noninductive heater (H) and a platinum resistance thermometer (PT$_1$). Another platinum resistance thermometer (PT$_2$) measures the sample temperature. The sample temperature was scanned at the rate of 2 mK/sec and the capacitance values were recorded at intervals of 4 sec using
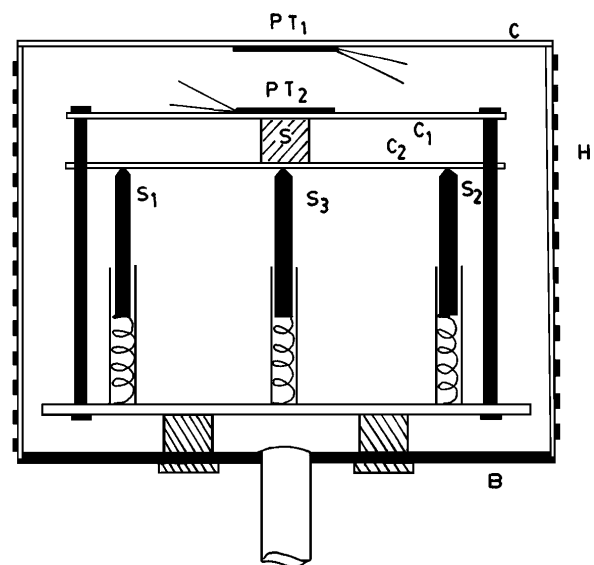

FIG. 1. Schematic diagram of three-terminal capacitance cell used for thermal expansion measurements.

a three-terminal capacitance bridge (Andeen Hagerling, Model 2500A) at a fixed frequency of 1 kHz. An average of fifty readings was taken to get the capacitance variation with temperature at 0.4 K intervals. An alloy sample of Fe–25 at. % Al composition was prepared from 99.99% purity metals by arc melting under an argon atmosphere in an Edmund Bühler D-7400 arc melting furnace. A sample of cuboid shape, $3 \times 2 \times 2$ mm^3 in dimensions, was cut from the arc melted ingot. It was quenched from 1473 K by dropping into liquid nitrogen in an attempt to get chemical disorder. However, because of the bulk nature of the sample it was not possible to get a fully disordered alloy sample. The sample passes through the temperature range 1073–773 K where the equilibrium state is $B2$ order and below 773 K where the equilibrium state is $D0_3$. The x-ray diffraction pattern for the quenched sample shows lines corresponding to the $B32$ phase which could arise from very small antiphase domains of either $D0_3$ or $B2$ order [16]. However, because of the requirement of the bulk sample in our thermal expansion measurement we assume the quenched alloy to be disordered, although it may have slight incipient order. After completing measurements on this sample it was ordered by annealing at 773 K for 24 h followed by 723 K for one week. Thermal expansion measurements were then carried out on this $D0_3$ ordered sample. Figure 2 shows the observed temperature dependence of the fractional length change $\Delta L/L(T_0) = [L(T) - L(T_0)]/L(T_0)$ where the reference temperature $T_0 = 293$ K, for disordered and $D0_3$ ordered Fe$_3$Al in the temperature range 80–300 K together with the previously reported data [17] recorded at higher temperatures (300–1273 K). The equilibrium state of Fe$_3$Al below 823 K is $D0_3$ ordered, it changes to $B2$ order above 823 K, and a
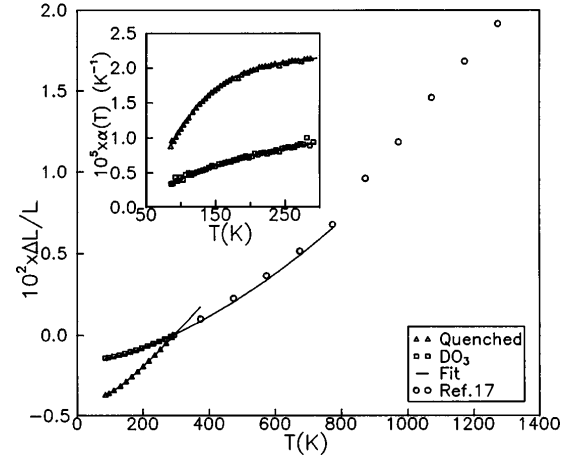

FIG. 2. Fractional length change data of ordered and disordered Fe$_3$Al and fits using Eq. (6). The inset shows the measured thermal expansion coefficient (α). The solid line in the inset shows the analytic derivative of Eq. (6).

disordered structure is obtained above 1073 K. The high temperature data [17] show discontinuities in $\Delta L/L(T_0)$ at about these temperatures, reflecting changes in the state of order. In our study we have retained the high temperature disordered state by quenching from above 1073 K and measured the thermal expansion of the disordered sample in the temperature range 80–300 K. Data for the ordered alloy are also recorded in the same temperature range, and a direct comparison between the ordered and disordered states of the alloy is therefore possible.

To calculate the thermal expansion of a solid theoretically one normally considers [18] three- and four-phonon interactions given by

$$\mathcal{H}' = \frac{1}{3!} \sum_{qq'q''} \sum_{jj'j''} \frac{h^{3/2}}{2^{3/2}N^{1/2}} \frac{\phi(\vec{q}j, \vec{q}'j', \vec{q}''j'')}{\sqrt{\omega_{qj}\omega_{q'j'}\omega_{q''j''}}} \delta_{\vec{q}+\vec{q}'+\vec{q}'', \vec{\mathcal{K}}_m} \times (a^\dagger_{-\vec{q}j} + a_{\vec{q}j})(a^\dagger_{-\vec{q}'j'} + a_{\vec{q}'j'})(a^\dagger_{-\vec{q}''j''} + a_{\vec{q}''j''}), \quad (2)$$

$$\mathcal{H}'' = \frac{1}{4!} \sum_{qq'q''q'''} \sum_{jj'j''j'''} \frac{h^2}{4N} \frac{\phi(\vec{q}j, \vec{q}'j', \vec{q}''j'', \vec{q}'''j''')}{\sqrt{\omega_{qj}\omega_{q'j'}\omega_{q''j''}\omega_{q'''j'''}}} \delta_{\vec{q}+\vec{q}'+\vec{q}''+\vec{q}''', \vec{\mathcal{K}}_m}$$
$$\times (a^\dagger_{-\vec{q}j} + a_{\vec{q}j})(a^\dagger_{-\vec{q}'j'} + a_{\vec{q}'j'})(a^\dagger_{-\vec{q}''j''} + a_{\vec{q}''j''})(a^\dagger_{-\vec{q}'''j'''} + a_{\vec{q}'''j'''}), \quad (3)$$

where $a^\dagger_{\vec{q}j}$ ($a_{\vec{q}j}$) is the creation (annihilation) operator for a phonon of the jth branch, wave vector $\vec{q}$, and frequency $\omega_{\vec{q}j}$, Φ's are related to the atomic force constant tensors, $\vec{\mathcal{K}}_m$ is a reciprocal lattice vector, and N is the number of allowed vectors. The free energy is then calculated within the framework of the Rayleigh-Schrödinger perturbation theory using $\mathcal{H}' + \mathcal{H}''$ as a perturbation, and finally the lattice constant is obtained as a function of temperature by minimizing the free energy with respect to it. This approach is, however, quite tedious and, in fact, only for a linear chain are explicit calculations usually available in the literature. We shall therefore follow here a rather simple-minded semiclassical approach

in which the effects of three- and four-phonon interactions will be simulated by considering the anharmonic potential $V(x) = cx^2 - gx^3 - fx^4$, where c, g, and f are constants, g and f measuring the strengths of the cubic and quartic anharmonicities, respectively. The x^3 term describes the asymmetry of the mutual ion-ion repulsive potential and the x^4 term takes care of the flattening of the bottom of the potential well which gives mode softening. Classically, the average lattice displacement at temperature T for the above potential can be calculated using the Boltzmann distribution [19]. We obtain

$$\langle x \rangle_T = \frac{3g}{4c^2}(k_BT)[1 - G(k_BT) - F(k_BT)^2] \quad (4)$$

where, $G = \frac{15}{16}\frac{g^2}{c^3} - \frac{8f}{c^2}$, $F = \frac{35}{16}(\frac{15}{4}\frac{g^2f}{c^5} + \frac{3f^2}{c^4})$ and terms higher than cubic in (k_BT) have been neglected. In our present semiclassical scheme we replace the classical thermal energy k_BT by the average energy of a quantum oscillator. We use the Debye model for the acoustic phonons and the Einstein approximation for the optical modes and also include the electronic contribution to the average lattice displacement which then assumes the following expression

$$\langle x \rangle_T = \frac{\gamma}{2}T^2 + \frac{3g}{4c^2}[\epsilon - G\epsilon^2 - F\epsilon^3] \qquad (5)$$

where

$$\epsilon = \left\{ \left(\frac{3}{p}\right)3k_BT\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{z^3\,dz}{e^z - 1} \right.$$
$$\left. + \left(\frac{p-3}{p}\right)\frac{k_B\Theta_E}{e^{\Theta_E/T} - 1} \right\}$$

and γ gives a measure of the electronic contribution to the lattice displacement [20], Θ_D and Θ_E are, respectively, the Debye and Einstein temperatures, and p is the average number of phonon branches actually excited over the entire range of temperature. The fractional length change is now calculated as

$$\frac{\Delta L}{L(T_0)} = \frac{\langle x \rangle_T - \langle x \rangle_{T_0}}{x_0}, \qquad (6)$$

to which the experimentally obtained fractional length change data are then fitted using $g' = g/c^2x_0$, $f' = f/c^2$, $g'' = g^2/c^3$, Θ_D, Θ_E, p, and γ as parameters. Here x_0 is the interatomic separation at $T = T_0$.

The difference in vibrational entropy between the ordered and disordered states of an alloy is finally estimated using the knowledge of the anharmonicity parameters and the characteristic temperatures (Θ_D and Θ_E) determined from the thermal expansion measurement. For the anharmonic potential $V(x)$, the specific heat (at constant volume) is obtained as

$$C_V = \frac{d}{dT}\left\langle \frac{P^2}{2m} + V(x) \right\rangle$$
$$= 3N\epsilon' - 6N\left(\frac{15g^2}{8c^3} - \frac{3f}{4c^2}\right)\epsilon \times \epsilon', \qquad (7)$$

where

$$\epsilon' = \left\{ \left(\frac{3}{p}\right)3k_B\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{z^4e^z}{(e^z - 1)^2}\,dz \right.$$
$$\left. + \left(\frac{p-3}{p}\right)k_B\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2} \right\}.$$

The vibrational entropy difference ΔS_{vib} between two phases of an alloy is now given by

$$\Delta S_{vib}(T) = \int_0^T \frac{\Delta C_V}{T}\,dT, \qquad (8)$$

where ΔC_V is the difference in the specific heat between the two phases at a temperature T.

To examine the accuracy of our thermal expansion measurements and the validity of our theoretical analysis we first make measurements on Al and fit these data and the standard data [21] of Cu to Eq. (6). The fits are found to be excellent and in Table I we compare the values of the parameters γ and Θ_D obtained from our fitting with those quoted in the literature [22,23]. The agreement is quite impressive, which imparts a fair amount of confidence in our approach. Figure 2 shows the fits to our experimentally obtained thermal expansion data for the disordered and $D0_3$ ordered Fe_3Al alloys. Table I gives the values of the parameters that give the best fits. The percentage rms deviation is found to be 0.2 for both the fits. It is evident from the figure that the data for the $D0_3$ ordered Fe_3Al in the temperature range 80–300 K match quite smoothly with the data at high temperatures [17]. In fact, the extrapolated curve obtained from Eq. (6) with the same parameter values as used in the fitting of $D0_3$ phase data (in the range 80–300 K) agrees very well with the high temperature data [17] up to 823 K, the temperature of phase transformation from $D0_3$ to $B2$ phase. The inset in Fig. 2 shows the variation of thermal expansion coefficient $\{\alpha = (\Delta L/\Delta T)[1/L(T_0)]\}$ as a function of temperature as obtained directly from our measured fractional length change data by numerical differentiation. The solid line through the data is obtained by analytically differentiating Eq. (6) with respect to temperature, using for $\langle x \rangle_T$ our theoretical expression (5) with the same parameter values as obtained by fitting the fractional length change data to Eq. (6).

TABLE I. Values of anharmonicity parameters and characteristic temperatures obtained by fitting fractional length change data to Eq. (6). The values of Θ_D and γ shown in the curly braces are reported values from specific heat data [22,23].

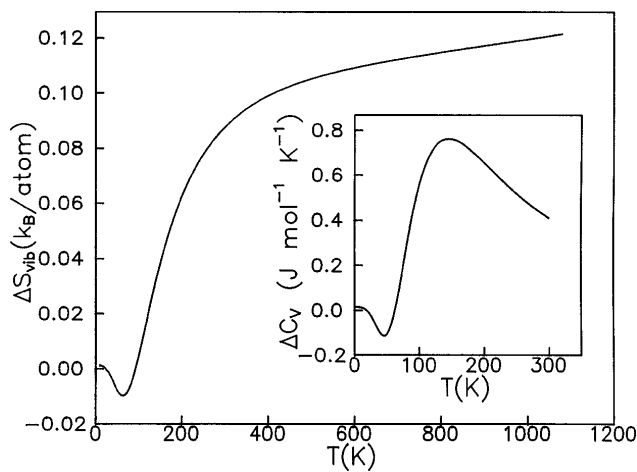| Sample	g' (eV^{-1})	g'' (eV^{-1})	f' (eV^{-1})	Θ_D (K)	γ (K^{-2})
Copper	0.265 ± 0.008	$(8.86 \pm 0.21) \times 10^{-6}$	$(1.04 \pm 0.02) \times 10^{-6}$	344.5 ± 0.8 $\{345\}$	$(2.60 \pm 0.08) \times 10^{-10}$ $\{2.54 \times 10^{-10}\}$
Aluminum	0.370 ± 0.004	$(7.85 \pm 1.31) \times 10^{-6}$	$(9.20 \pm 1.53) \times 10^{-7}$	423.3 ± 0.4 $\{428\}$	$(9.13 \pm 0.04) \times 10^{-10}$ $\{9.20 \times 10^{-10}\}$
Fe_3Al (quenched)	0.431 ± 0.003	$(2.22 \pm 0.03) \times 10^{-3}$	$(2.57 \pm 0.03) \times 10^{-4}$	431.0 ± 0.3	$(-1.58 \pm 0.03) \times 10^{-8}$
$Fe_3Al(D0_3)$	0.100 ± 0.002	$(4.66 \pm 0.02) \times 10^{-3}$	$(5.34 \pm 0.02) \times 10^{-4}$	376.7 ± 0.3	$(1.27 \pm 0.02) \times 10^{-8}$

FIG. 3.   The variation of ΔS_{vib} and ΔC_V (inset) for Fe_3Al as a function of temperature.

The thermal expansion data for disordered Fe_3Al could be fitted well with only three acoustic branches ($p = 3$) and $\Theta_D = 431$ K ($\nu_D = 8.98$ THz). Fits carried out with the Einstein term present and a variable p yielded $p = 3$, thereby showing the absence of the optical modes. In the case of $D0_3$ ordered Fe_3Al, however, both acoustic and optical modes were required to fit the data with a value of p close to 4, which suggests that in the $D0_3$ ordered phase an optical phonon branch develops together with the three acoustic branches. The values of Θ_D and Θ_E were obtained in this case as 376.7 K ($\nu_D = 7.85$ THz) and 507.9 K ($\nu_E = 10.58$ THz), respectively, which are in remarkably good agreement with those determined from density-of-state (DOS) calculation by Fultz et al. [7] using Born–von Karman force constants as obtained by Robertson [24]. For disordered Fe_3Al the DOS curves are Debye-like with a maximum frequency of 8.8 THz, whereas for ordered Fe_3Al the maximum frequency of Debye-like modes decreases to 7.8 THz, but an additional peak is observed at a frequency of 10.8 THz. The presence of an additional Einstein frequency for ordered Fe_3Al has been physically attributed to the formation of sublattices in the $D0_3$ ordered structure, with one sublattice being rich in Al and having a lower mass and correspondingly a higher vibrational frequency.

In Fig. 3 we plot the temperature dependence of ΔS_{vib} and ΔC_V using Eqs. (7) and (8) with the same parameter values as given in Table I. The vibrational entropy difference at a temperature $T = 1073$ K comes out to be 0.113 k_B/atom which is in very good agreement with the value of 0.10 k_B/atom obtained by Fultz et al. [7] from differential scanning calorimetric measurements.

In conclusion, we would like to emphasize that thermal expansion measurements can serve as an effective ap-proach to study the changes in vibrational properties of alloys due to chemical order-disorder transformations. We show that this method can provide us with reliable esti-mates of characteristic temperatures (Θ_D and Θ_E), cubic and quartic anharmonicity parameters in the lattice poten-tial energy, and the vibrational contribution to entropy.

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