Vibrational Entropy of Ordered and Disordered Ni_3Al

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We have measured the difference in vibrational entropy of Ni_3Al in two states of chemical order: as a disordered fcc solid solution, and as the equilibrium $L1_2$ ordered structure. Data were obtained from three independent methods: low-temperature calorimetry, temperature-dependent x-ray diffractometry, and temperature-dependent extended electron energy-loss fine structure spectrometry. We estimate that at high temperatures, the vibrational entropy of chemically disordered Ni_3Al is $0.3k_B$/atom greater than for ordered Ni_3Al.

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Recently there has been rapid progress towards understanding the thermodynamics of chemical ordering in metallic alloys. There have been many attempts to obtain *ab initio* free energy functions, from which phase diagrams of stable and metastable phases can be obtained with better than qualitative success (e.g., [1]). The free energy comprises an enthalpy term obtained from electron energy calculations, and an entropy term obtained from the cluster variation method. This entropy is a configurational entropy, calculated with the combinatorics of arranging atoms on a crystal lattice, given a particular state of order. In the *ab initio* free energies, the difference in the vibrational entropy of two phases is usually neglected, although it has been included with the Debye-Grüneisen approximation [2].

It has been known for some time that the entropies of mixing for concentrated solid and liquid solutions are larger than predicted from configurational entropy alone [3], and the solubility limits of dilute solutions show similar discrepancies [4]. There is only weak experimental evidence for the importance of vibrational entropy for order-disorder transformations, however [5–7]. Most evidence is theoretical [8–13]. For example, the mean field approximation for the free energy of an equiatomic binary A-B alloy can be extended to include vibrational entropy with the Einstein model. Doing so requires different vibrational frequencies for A-A, B-B, and A-B pairs of atoms, denoted ω_{AA}, ω_{BB}, and ω_{AB}, and we must account for how an increase in the long-range order parameter causes the replacement of A-A and B-B pairs with A-B pairs. Minimizing the free energy with respect to the long-range order parameter L provides the following relationship at high temperatures:

$$L=\frac{2k_BT}{z(V_{AA}+V_{BB}-2V_{AB})}\ln\left[\frac{1+L}{1-L}\left(\frac{\omega_{AB}^2}{\omega_{AA}\omega_{BB}}\right)^{3/2}\right]. \tag{1}$$

This is the well-known Bragg-Williams result, with the addition of a frequency factor. Here z is the lattice coordination number, and the chemical energy for preference of like pairs of atoms, $V_{AA}+V_{BB}-2V_{AB}$, is positive for alloys that develop order. For an ordering alloy, we expect the A-B bonds to be stiffer than the A-A and B-B bonds (i.e., $\omega_{AB}^2>\omega_{AA}\omega_{BB}$). At finite temperatures, the lower vibrational entropy of the ordered state will destabilize it with respect to the disordered state, and the critical temperature for ordering will be suppressed [14]. It has been argued that including vibrational entropy in the free energy can cause a substantial suppression of the critical temperature, even by a factor of 2 [8–10,13].

If we go beyond the Einstein approximation and compare a state, α, of a material having the $3N$ normal modes $\{\omega_1^\alpha,\omega_2^\alpha,\ldots,\omega_{3N}^\alpha\}$ to another state β, the difference in vibrational entropy at high temperatures, ΔS_v, is

$$\Delta S_v\equiv\Delta S_v^\beta-\Delta S_v^\alpha=k_B\ln\left(\frac{\prod_{i=1}^{3N}\omega_i^\alpha}{\prod_{j=1}^{3N}\omega_j^\beta}\right). \tag{2}$$

If the vibrational frequencies of a disordered (D) alloy are all in the same ratio to those of an ordered (O) alloy, Eq. (2) reduces to a logarithmic ratio of the Debye (or Einstein) temperatures θ:

$$\Delta S_v\equiv S_v^D-S_v^O=3Nk_B\ln\left(\frac{\theta^O}{\theta^D}\right). \tag{3}$$

In our experimental measurements on Ni_3Al with the extended electron energy-loss fine structure (EXELFS) technique, we obtained characteristic vibrational frequencies of the two atomic species in the two states (disordered and ordered) of the material. Equation (3) becomes

$$\Delta S_v=3Nk_B\ln\left[\left(\frac{\theta_{\rm Ni}^O}{\theta_{\rm Ni}^D}\right)^{3/4}\left(\frac{\theta_{\rm Al}^O}{\theta_{\rm Al}^D}\right)^{1/4}\right]. \tag{4}$$

Equations (3) and (4) are valid if the phonon dispersion curves of ordered and disordered alloys differ only in scale, and not in shape. While this is unlikely in detail, we may expect Eqs. (3) and (4) to be qualitatively useful.

Here we report experimental measurements of the difference in vibrational entropy of an ordered and a disordered alloy. The material is Ni_3Al, which assumes the $L1_2$ ordered structure in thermodynamic equilibrium.

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We have recently prepared this alloy as a disordered fcc solid solution by physical vapor deposition onto cold substrates [15], and we used these evaporated films in the present study. Samples with $L1_2$ order were obtained by annealing these same films at about 400 °C for 10 to 30 min. The ordered and disordered states were confirmed by x-ray diffraction. We used three independent experimental techniques to measure the vibrational entropy difference of ordered and disordered Ni_3Al.

The first and most direct method involved measuring the difference in heat capacity of the two states of the material, $\Delta C_p \equiv C_p^D - C_p^O$, from 63 to 343 K, and then calculating

$$\Delta S_v(T) = \int_{63\,\mathrm{K}}^{T} \frac{\Delta C_p}{T'} dT' . \tag{5}$$

Low-temperature heat capacity measurements were obtained using a Perkin Elmer DSC-4 differential scanning calorimeter (DSC) that had been modified with its sample holder installed in a liquid helium Dewar. Equal masses (27.7 mg) of the disordered and ordered Ni_3Al materials were placed in the two sample pans of the DSC. Heat capacity measurements comprised pairs of runs, with the two samples interchanged in their sample pans between runs. The difference in heat capacities of the two samples was obtained from the difference of these two sets of runs. Additional calibration runs were carried out using a NIST sapphire standard of known heat capacity. A scan rate of 20 $\mathrm{K\,min^{-1}}$ was used throughout. To counteract instrumental drift, runs were made in short, overlapping scans over temperature ranges of 60 K each.

Figure 1 presents the indefinite integral of Eq. (5) as a function of T. In addition to the experimental data, the figure also presents the best fit to an integral of the difference between two Debye functions with $\theta_D = 452$ and 495 K. Using Eq. (5) over the temperature range of the experimental data gives a rigorous lower bound on $\Delta S_v = +1.62\ \mathrm{J\,mol^{-1}\,K^{-1}}$ or $+0.19 k_B$/atom. Using the Debye model fit over the temperature range from 0 K to the critical temperature of about 1700 K [16] gives $\Delta S_v = +0.27 k_B$/atom.

The second method for measuring the difference in vibrational entropy was a measure of x-ray Debye-Waller factors. X-ray diffraction patterns were obtained with Mo $K\alpha$ radiation and an Inel CPS-120 position-sensitive detector spanning 120° in 2θ angle. Data were acquired at room temperature and at liquid nitrogen temperature for samples of the as-evaporated Ni_3Al, and material after annealing. The temperature dependence of the intensities of the diffraction peaks of various order were fitted to a Debye-Waller model. This procedure resulted in Debye temperatures around 600 K, but differing by 50 to 100 K. Equation (3) gives a difference in vibrational entropy of $\Delta S_v = +0.3$ to $+0.7 k_B$/atom.

The third method was a measure of local vibrational characteristics, specifically the mean-square relative displacements (MSRD) of Ni and Al atoms with respect to their first nearest neighbors. The technique was extended electron energy-loss fine structure (EXELFS) [17,18], performed at temperatures from 100 to 300 K. Al K-edge and Ni L_{23}-edge electron energy-loss spectra were acquired with a Gatan 666 parallel-detection magnetic prism spectrometer attached to a Philips EM 430 transmission electron microscope. Channel-to-channel fluctuations in the detector system were removed by direct normalization with a uniform illumination spectrum, followed by gain averaging over several spectra [19]. To remove the smoothly varying portion of the energy-loss data, we used cubic polynomial spline fits with knots separated approximately evenly in k space. The EXELFS oscillations were normalized to theoretically calculated energy-differential cross sections [20], which were scaled to match the measured edge jump heights. Figure

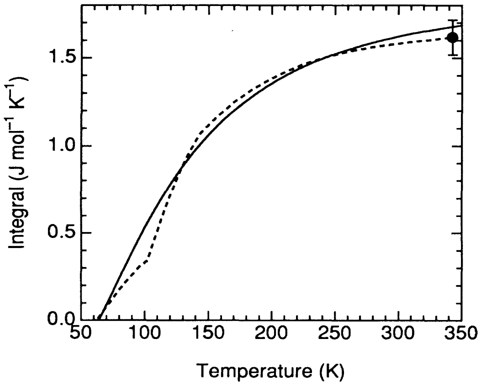

FIG. 1. Indefinite integral of Eq. (5) as a function of T (dashed curve) and least-squares fit using a difference of two Debye functions with $\theta_D = 452$ and 495 K (solid curve). The error bar indicates the cumulative error in the integral at the upper temperature limit of 343 K.

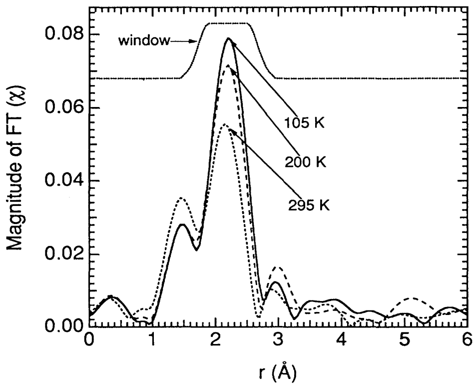

FIG. 2. Fourier band-pass filtering of Al K-edge EXELFS data from disordered Ni_3Al. Data in the range $4.0 < k < 10.0$ $\mathrm{\AA^{-1}}$ were Fourier transformed. The band-pass filter for extracting EXELFS oscillations from the first-nearest-neighbor shell is shown at the top.

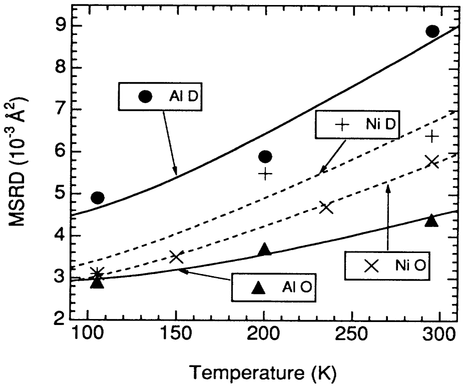

FIG. 3. MSRD data and fits to the Einstein model for Al and Ni atoms in disordered and ordered Ni_3Al.

2 presents typical radial distribution functions, uncorrected for phase shifts, from the Al *K*-edge EXELFS data from disordered Ni_3Al. The band-pass filter for extracting the EXELFS oscillations from the first-nearest-neighbor shell is shown at the top of the figure.

By comparing the filtered oscillations, changes in MSRD were determined relative to the lowest-temperature datum. The MSRD data were fitted to predictions of the Einstein model [21], allowing the lowest-temperature MSRD to vary. Einstein temperatures obtained were 312 K (+34 K,−25 K) for Al atoms in disordered Ni_3Al, 453 K (+31 K, − 20 K) for Al atoms in ordered Ni_3Al, 279 K (+49 K, −31 K) for Ni atoms in disordered Ni_3Al, and 304 K (+6 K, −7 K) for Ni atoms in ordered Ni_3Al. The MSRD data and their Einstein temperature fits are presented in Fig. 3. There is a strong reduction in the vibrational amplitude of Al atoms in the ordered material, and this change is measured reliably. The reduction in vibrational amplitude of Ni atoms is much smaller and is less reliable. By substituting the Einstein temperatures for the Al atoms and Ni atoms into Eq. (4), we obtain $\Delta S_v = +0.47(+0.27, -0.41) k_B$/atom. The large errors originate from the relative inaccuracy of the MSRD data for Ni atoms.

In summary, we have performed three independent experiments on the vibrational entropy of disordered and $L1_2$-ordered Ni_3Al. All three show that the vibrational entropy of the disordered state is greater than the ordered state. Considering the characteristics and accuracies of the techniques, we estimate that $\Delta S_v = +0.3(\pm 0.1) k_B$/atom. While this is less than the configurational entropy of mixing ($+0.56 k_B$/atom), it is large enough to affect substantially the relative thermodynamic stabilities of the disordered and ordered states of Ni_3Al. From our temperature-dependent EXELFS measurements, we find that the Al atoms undergo larger changes in vibrational amplitudes than do the Ni atoms.

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