An Inelastic Nuclear Resonant Scattering Study of Partial Entropies of Ordered and Disordered Fe$_3$Al

B. FULTZ*, W. STURHAHN**, T. S. TOELLNER** and E. E. ALP**
* Div. Engineering and Applied Science, 138-78, California Institute of Technology, Pasadena, California 91125, btf@hyperfine.caltech.edu
** Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439

ABSTRACT

Inelastic nuclear resonant scattering spectra were measured on alloys of Fe$_3$Al that were chemically disordered, partially-ordered, and D0$_3$-ordered. The phonon partial DOS for $^{57}$Fe atoms were extracted from these data, and the change upon disordering in the partial vibrational entropy of Fe atoms was obtained. By comparison to previous calorimetry measurements, it is shown that the contribution of the Fe atoms to the vibrational entropy is a factor of 10 smaller than that of the Al atoms. With the assistance of Born - von Kármán model calculations on the ordered alloy, it is shown that differences in the vibrational entropy originate primarily with changes in the optical modes upon disordering. The phonon DOS of $^{57}$Fe was found to change systematically with chemical short range order in the alloy. It is argued that changes in the vibrational entropy originate primarily with changes in the chemical short-range order in the alloy, as opposed to long-range order.

INTRODUCTION

Vibrational Entropy

Phase diagrams of materials have been the subject of extensive experimental and theoretical research. In recent years, free energies of solid phases have been calculated by elegant combinations of methods for calculating the electronic energy with the local density approximation and methods using cluster approximations for calculating the configurational entropy [1,2]. The change in vibrational entropy during a solid state phase transition is often thermodynamically important, however [3-8]. It is now accepted that vibrational entropy must be considered in alloy thermodynamics. Recent work has focused on the reasons underlying the differences in vibrational entropy of different states of materials [6-10].

Knowledge of the phonon density of states (DOS) is an important step towards the understanding of vibrational entropy. For alloys, however, the total phonon DOS masks important details. The different atomic species in an alloy are not expected to have identical motions. The partial phonon DOS, defined below, describes the spectrum of motions of the individual atoms in the alloy. Knowledge of the motions of individual atoms, rather than the overall vibrational spectrum, provides more of the information needed to identify reasons for the differences in vibrational entropy of alloy phases. In this paper we use knowledge of the $^{57}$Fe phonon partial DOS in Fe$_3$Al to show that the changes in vibrational entropy upon ordering are caused primarily by changes in the motions of Al atoms. Furthermore, we show that much of this change in the motion of Al atoms occurs in those phonons described as optical modes of the alloy.
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
**Inelastic Nuclear Resonant Scattering**

To date the most detailed information on phonons in solids has been obtained from studies on coherent inelastic neutron scattering by single crystals of pure elements or ordered compounds. The momentum and energy transfers between the neutron and the crystal are used to identify both the frequencies and wavevectors of phonon excitations in the solid. Unfortunately, for many interesting materials it is impossible to obtain single crystals for coherent inelastic neutron scattering experiments. This is especially true for materials far from thermodynamic equilibrium, highly disordered alloys for example, where the methods for preparing single crystals will destroy the interatomic disorder. Furthermore, interpreting the phonon frequencies from neutron groups measured on single crystals of disordered alloys is typically performed with a virtual crystal approximation, which is known to be unreliable [9]. For such materials it is appropriate to measure the spectrum of vibrational excitations, without information on the phonon wavevectors. An experimental advance towards more detailed data is to measure the phonon partial DOS for the individual atoms in an alloy.

A method using synchrotron radiation for measuring the phonon partial DOS in solids has been developed recently [11, 12]. The method evolved from studies on nuclear forward scattering of synchrotron radiation, which has been increasingly practical since 1985 [13]. (Reference [14] is a recent review of nuclear forward scattering.) Undulator-based third generation synchrotron sources have invigorated these applications of the Mössbauer effect. The Mössbauer effect is, by definition however, purely elastic scattering. Nevertheless, outside the narrow energy window for the Mössbauer effect itself, it is now possible to observe nuclear transitions that are accompanied by phonon creation or annihilation. This method of inelastic nuclear resonant x-ray scattering is similar to incoherent inelastic neutron scattering, where an elastic line is surrounded by inelastic intensity that can be used to obtain the phonon DOS of a material.

**PRINCIPLES**

**Partial Vibrational Entropy**

In the classical limit, vibrational entropy is related to the phonon DOS, $g(\varepsilon)$, as

$$S_{\text{vib}} = -3k_B \int_0^\infty g(\varepsilon) \ln \left( \frac{\varepsilon}{\varepsilon_0} \right) d\varepsilon \tag{1}$$

where $\varepsilon$ is the phonon energy, and $\varepsilon_0$ is a constant that will vanish when differences in entropy are calculated. The phonon DOS, $g(\varepsilon)$, is a spectrum of phonon frequencies, each of energy $\varepsilon_j$. In discrete form it is

$$g(\varepsilon) = \frac{1}{3N} \sum_j \delta(\varepsilon - \varepsilon_j) \tag{2}$$

Substituting Eq. 2 into 1 gives

$$S_{\text{vib}} = -\frac{k_B}{N} \int_0^\infty \sum_j \delta(\varepsilon - \varepsilon_j) \ln \left( \frac{\varepsilon}{\varepsilon_0} \right) d\varepsilon \tag{3}$$
For each phonon mode in the alloy, denoted, "j", we have a polarization vector, \( \mathbf{e}_{\xi,j} \), that describes the displacement and phase of the atom, \( \xi \), in the unit cell [15]. To ensure consistent amplitudes for all phonons, there must be a normalization of the polarization vectors for all atoms in the unit cell

\[
\sum_{\xi} |\mathbf{e}_{\xi,j}|^2 = 1
\]  

(4)

We therefore write:

\[
S_{\text{vib}} = -\frac{k_B}{N} \sum_{\xi} \sum_{j=0}^{3N} |\mathbf{e}_{\xi,j}|^2 \delta(\varepsilon - \varepsilon_j) \ln \left( \frac{\varepsilon}{\varepsilon_0} \right) d\varepsilon
\]  

(5)

To separate the contributions of individual atoms to the vibrational entropy, it is convenient to define a “phonon partial DOS” as

\[
g_{\xi}(\varepsilon) = \frac{1}{3N} \sum_{j} |\mathbf{e}_{\xi,j}|^2 \delta(\varepsilon - \varepsilon_j)
\]  

(6)

Recognizing the expression of Eq. 6 in Eq. 5, we see that Eq. 5 is a sum of partial entropy contributions, \( S_{\xi} \), from each atom, \( \xi \), in the unit cell

\[
S_{\xi} = -3k_B \int_{0}^{\infty} g_{\xi}(\varepsilon) \ln \left( \frac{\varepsilon}{\varepsilon_0} \right) d\varepsilon
\]  

(7)

The total vibrational entropy is the sum of partial entropies obtained from the phonon partial DOS’s

\[
S_{\text{vib}} = \sum_{\xi} S_{\xi}
\]  

(8)

Data Analysis

The phonon partial DOS of \({}^{57}\text{Fe}\), \( g_{\text{ph}}(\varepsilon) \), is obtained from the inelastic nuclear resonant scattering spectra by correcting for the thermal occupancies of phonon modes and multiphonon scattering. The measured scattering intensity, \( I(Q,\varepsilon) \), is a sum of resonant absorption processes, each accompanied by a different number of phonon creations or annihilations, \( I_n(Q,\varepsilon) \). (Here \( \varepsilon \) is the energy loss, and \( Q \) is the momentum transfer, which is 7.3 Å\(^{-1}\) for the 14.41 keV transition in \({}^{57}\text{Fe}\).) We use the definitions [16]

\[
\gamma_0 = \int_{0}^{\infty} \coth \left( \frac{\varepsilon}{2k_B T} \right) \frac{g_{\text{ph}}(\varepsilon)}{\varepsilon} d\varepsilon
\]  

(10)

\[
2W = \frac{(\hbar Q)^2}{2M} \gamma_0
\]  

(11)

\[
A_1(\varepsilon) = \frac{g_{\text{ph}}(\varepsilon)}{\gamma_0 \varepsilon \left( 1 - \exp \left( \frac{\varepsilon}{k_B T} \right) \right)}
\]  

(12)
The measured scattering intensity, \( I(Q, \varepsilon) \), is the sum of intensities from all phonon processes

\[
I(Q, \varepsilon) = \sum_n I_n(Q, \varepsilon) \tag{15}
\]

Our problem is to use the measured \( I(Q, \varepsilon) \) to isolate the single scattering profile, \( A_i(\varepsilon) \). A convenient approach was mentioned by M. Y. Hu, et al. [17]. This method automatically corrects for the instrument resolution, \( Z(\varepsilon) \), as obtained from the zero-loss peak. This resolution function, \( Z(\varepsilon) \), is convoluted with the scattering from the specimen

\[
I(Q, \varepsilon) = Z(\varepsilon) \ast \left( e^{-2W} + \sum_n I_n(Q, \varepsilon) \right) \tag{16}
\]

The first term in the braces is the zero loss peak, reduced by the Debye-Waller factor. Taking the Fourier transform, \( \mathcal{F} \), of Eq. 16 simplifies the convolutions of Eq. 13, which become multiplications in Fourier space.

\[
\mathcal{F}[I(Q, \varepsilon)] = \mathcal{F}[Z(\varepsilon)] e^{-2W} \left( 1 + \sum_n \frac{(2W)^n}{n!} (\mathcal{F}A_i(\varepsilon))^n \right) \tag{17}
\]

The term in braces on the right side of Eq. 17 is recognized as the expansion of an exponential function

\[
\mathcal{F}[I(Q, \varepsilon)] = \mathcal{F}[Z(\varepsilon)] e^{-2W} \left( e^{2W \mathcal{F}A_i(\varepsilon)} \right) \tag{18}
\]

To isolate the single scattering profile, \( A_i(\varepsilon) \), we take the logarithm of Eq. 18, rearrange, and perform the inverse transformation, \( \mathcal{F}^{-1} \). If we neglect the normalization of the single scattering profile, and if we delete the spike at zero energy (which is suppressed by the thermal correction of Eq. 12 anyway), we obtain

\[
A_i(\varepsilon) = \mathcal{F}^{-1} \left[ \ln \left( \frac{\mathcal{F}[I(\varepsilon)]}{\mathcal{F}[Z(\varepsilon)]} \right) \right] \tag{19}
\]

The 2W is exponentiated to form the Debye-Waller factor, \( A_i(\varepsilon) \) is the single scattering profile, and \( A_n(\varepsilon) \) is the scattering profile for the creation of n phonons.

Extracting the phonon partial DOS, \( g_n(\varepsilon) \), is the goal of our data analysis. We can do this easily with Eq. 12 once we know the single scattering profile, \( A_i(\varepsilon) \). This requires that the experimental spectra are corrected for multiphonon scattering. For fixed values of \( Q \) and temperature, the energy dependence of the various phonon contributions, \( I_n(Q, \varepsilon) \), is
Data analysis therefore proceeds as follows. After subtraction of a constant background of order 0.01 Hz, the zero loss profile, \( Z(\varepsilon) \), is identified in the measured spectrum. This elastic peak is subtracted from the data, and Eq. 19 is used to obtain the single scattering profile, \( A_{ss}(\varepsilon) \). The single scattering profile is easily converted into the phonon partial DOS, \( g_{\text{ph}}(\varepsilon) \), with Eq. 12. This data analysis procedure is performed with the software package PHOENIX, written by W. Sturhahn, which provides other analyses of the inelastic scattering and tests the reliability of the experimental spectra.

EXPERIMENTAL

The measurements were performed at the 3-ID undulator beamline of the Advanced Photon Source. A premonochromater consisting of water-cooled diamond (111) crystals in a nondispersive setting produced a beam of 14.413 keV synchrotron radiation with an energy bandwidth of 1.2 eV. Further monochromatization to an 875 \( \mu \)eV bandwidth was provided by a high-resolution monochromater [18], comprising two asymmetrically-cut silicon (975) crystals in a dispersive geometry. The photon flux incident on the foil sample within this bandwidth was \( 6 \times 10^9 \) Hz. The energy alignment of the high-resolution monochromater was tuned around the nuclear resonance in steps of 300 \( \mu \)eV. An avalanche photodiode with an active area of 2 cm\(^2\) was mounted 4 mm above the specimen and used to detect K-shell internal conversion x-rays of 6.4 keV. To suppress the x-ray fluorescence processes excited by the synchrotron flash, data were acquired approximately 30 ns after the flash. All measurements were performed at room temperature.

Measurements were performed on three foils of \(^{57}\)Fe\(_3\)Al of 3 \( \mu \)m thickness. They were prepared by arc-melting a 50 mg ingot under an argon atmosphere, followed by piston-anvil quenching into a thin foil and cold rolling. A JEOL Superprobe 733 electron microprobe was used to check for chemical heterogeneities, and to determine that the chemical composition of the foil was Fe-26.0 at.\% Al. One specimen was used directly in this state, and is denoted the “disordered” sample. A second foil of \(^{57}\)Fe\(_3\)Al was annealed at 473 K for 1 h to induce partial chemical order, and is denoted the “partially-ordered” sample. The third foil of \(^{57}\)Fe\(_3\)Al was annealed at 773 K for 6 days, followed by 723 K for 40 days, and is denoted the “ordered” sample. The states of chemical long-range order (LRO) of the three samples of \(^{57}\)Fe\(_3\)Al were determined by x-ray diffractometry and by conversion electron Mössbauer spectrometry. Some x-ray diffraction patterns are presented in Fig. 1. Only the “ordered” sample shows any \( D_0 \), LRO, as evidenced by intense (1/2 1/2 1/2) and (100) x-ray superlattice diffractions. The diffraction pattern from the partially-ordered sample may show some broad intensity from about 28 - 37 degrees that could be diffuse scattering originating with chemical short-range order (SRO).

Fig. 1 X-ray diffraction patterns (Co K\(\alpha\) radiation, Debye-Scherrer optics) from the three specimens of \(^{57}\)Fe\(_3\)Al, scaled for equal intensities of the (110) fundamental diffraction at 52°.
Conversion electron Mössbauer spectrometry was used to measure the chemical short range order in the samples (Fig. 2). A perfect state of D0$_{2}$, chemical order would have Fe atoms with only 0 or 4 Al neighbors (the 4[b] and 8[c] sites in Wyckoff notation) in a 1:2 ratio. The excess of Fe atoms with 3 Al neighbors in our ordered sample indicates a LRO parameter between 0.7 and 0.8 (where perfect D0$_2$ order would be 1.0). The disordered sample shows a much broader distribution of local chemical environments, peaking at 2 nn Al atoms as expected for a random solid solution. For the disordered alloy, the probability of finding an Fe atom with the number, n, of nn Al atoms follows approximately the binomial distribution [19], although there was a small excess of Fe atoms with 4 Al neighbors. The partially-ordered sample shows an HMF distribution that is intermediate between the ordered and disordered alloy.

Local vibrational amplitudes of the Fe atoms and Al atoms with respect to their nn atoms were measured with extended electron energy loss fine structure spectrometry (EXELFS) [9,21,22], performed at temperatures ranging from 100 K to 420 K. The Al K-edge and Fe L$_{3}$-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. Processing of the spectra to obtain EXELFS oscillations and radial distribution functions (RDF's) followed procedures described elsewhere [5,9,21,22].

RESULTS

Experimental Phonon Partial DOS

Inelastic nuclear resonant scattering spectra are presented in Fig. 3. The Mössbauer elastic peak at $\varepsilon = 0$ meV is surrounded by the inelastic contribution from nuclear resonant photon absorptions accompanied by phonon excitation (right), and phonon absorption (left). The vibrational modes around 43 meV are present in the disordered alloy, but show a distinct growth in intensity with the chemical order in the alloy. The non-zero intensity at energies above 50 meV is primarily multiphonon scattering [16,23]. We corrected for the multiphonon scattering by the Fourier-logarithm deconvolution method described above, and by an iterative procedure [24]. For comparison, the two phonon scattering profile calculated with the iterative procedure is shown in Figure 4 together with the experimental spectrum. These spectra were converted into phonon partial DOS curves for $^{57}$Fe, and results are shown at the bottom of Fig. 5.
Fig. 3. Conversion x-ray intensity versus photon energy from the disordered, partially-ordered, and ordered alloys near the elastic (Mössbauer) resonance set at 0 meV. Curves for the partially-ordered and ordered samples are shifted vertically by factors of 10 and 100, respectively.

Fig. 4. Experimental spectrum of 3, together with the 2-phonon contribution to the scattering.

Fig. 5. Phonon partial DOS curves for $^{57}$Fe in $^{57}$Fe$_2$Al. Top: calculated curves using interatomic force constants for the alloys with disorder and D0$_3$ chemical order [7]. Bottom: experimental phonon partial DOS curves obtained from the spectra of Fig. 3.
We employed a Born-von Kármán model to calculate the phonon densities of states (DOS) using the force constants of van Dijk [25]. The dynamical matrix was diagonalized for about $10^7$ values of $k$ in the first Brillouin zone, and histogram binning of the eigenfrequencies was used to obtain the phonon DOS $g(\varepsilon)$. For each eigenmode, four other histograms were prepared with weights provided by the square of the polarization vectors, $|e_i|^2$, so the phonon partial DOS curves were obtained from the Al atoms, the Fe 4[b] atoms, and the Fe 8[c] atoms (the latter were represented by two of the four $\xi$ in Eq. 6). These results are shown in Fig. 6, and at the top of Fig. 5 (where they are convoluted with a Gaussian function of 850 $\mu$eV full-width-at-half-maximum to account approximately for the resolution of the monochromator). The partial DOS curve for the disordered alloy was calculated with force constants obtained from bcc dispersion curves [26], which implicitly assumes that the alloy contains one species of atom with the average mass of Fe and Al. This virtual crystal approximation is intrinsic to the analysis of coherent inelastic neutron scattering experiments on disordered alloys when single phonon frequencies are used to parameterize the neutron spectra measured at constant $Q$. The virtual crystal calculation has particularly poor agreement with the experimental data from the disordered alloy for energies above 34 meV in the range of the optical modes of the ordered alloy. On the other hand, for D03-ordered Fe$_3$Al we find good agreement between the calculated partial DOS and our experimental data (where the calculated curve is the sum of two partial DOS curves for the 4[b] and 8[c] crystallographic sites, shown as dashed lines at the top of Fig. 5). The only distinct discrepancy occurs around 26 meV, although this discrepancy vanishes if the calculated curves are broadened by about 2 meV. The experimental data also show intensity in the energy gap around 34 - 38 meV owing to some disorder in the ordered alloy. The intensity in this energy gap becomes larger for the partially-ordered and disordered alloys. With increasing disorder there is a decrease in intensity of the DOS at optical mode energies, and these modes also decrease in energy.
VIBRATIONAL ENTROPY

Comparison with Calorimetry

With Eq. 7 we use the phonon partial DOS curves, \( g_{\text{Fe}}^{\text{ph}}(\epsilon) \) and \( g_{\text{Al}}^{\text{ph}}(\epsilon) \), to obtain \( \Delta S^{\text{vib}}_{\text{Fe}} = S^0_{\text{Fe}} \). The data of Fig. 5 provide \( \Delta S^{\text{vib}}_{\text{Fe}} = (+0.01 \pm 0.005) \ \text{K}_\text{b} \ (\text{Fe atom})^{-1} \). Data from two other sets of runs with a lower resolution 5 meV monochromator gave \( \Delta S^{\text{vib}}_{\text{Fe}} = -0.02 \ \text{K}_\text{b} \ (\text{Fe atom})^{-1} \). These data show that \( \Delta S^{\text{vib}}_{\text{Fe}} \) is small.

The difference in total vibrational entropy of disordered and ordered \( \text{Fe}_3\text{Al}, \Delta S^{\text{vib}} = S^0 - S^0 \), is much larger than this small contribution from Fe atoms. This total entropy difference, \( \Delta S^{\text{vib}} = S^0 - S^0 \), is the sum of contributions from the Fe atoms and the Al atoms (c.f. Eq. 8). The present results on \( S^0_{\text{Fe}} \) and \( S^0_{\text{Al}} \) provide direct information on the roles of Fe atoms, but the role of Al atoms can be deduced because the total vibrational entropy difference, \( \Delta S^{\text{vib}} \), has been measured previously by calorimetry, and is \( \Delta S^{\text{vib}} = (+0.1 \pm 0.03) \ \text{K}_\text{b} \ \text{atom}^{-1} \) [6]. Since the partial entropies of Fe and Al are added to obtain \( \Delta S^{\text{vib}} \), we use Eq. 8 in the form: \( \Delta S^{\text{vib}}_{\text{Fe}} = 0.75 \Delta S^{\text{vib}}_{\text{Fe}} + 0.25 \Delta S^{\text{vib}}_{\text{Al}} \), where \( \Delta S^{\text{vib}}_{\text{Fe}} \) and \( \Delta S^{\text{vib}}_{\text{Al}} \) are the change in entropy upon disordering per Fe and per Al atom. We find \( \Delta S^{\text{vib}}_{\text{Fe}} = 0.37 \ \text{K}_\text{b} \ \text{atom}^{-1} \). Evidently the difference in vibrational entropy of disordered and ordered \( \text{Fe}_3\text{Al} \) is due primarily to changes in the vibrations of Al atoms.

Comparison with EXELFS

Previously reported EXELFS data [2,9] also show that the Al atoms are primarily responsible for the difference in vibrational entropy of ordered and disordered \( \text{Fe}_3\text{Al} \). In this study the temperature dependence of the EXELFS oscillations was measured for both the Fe and Al K-edges at temperatures from 97 to 400 K. By comparing the 1nn oscillations in the Fourier transform of the EXELFS data, changes in the mean-squared relative displacements (MSRD) measured from the Al K-edge (Al MSRD) and the Fe L2,3-edge (Fe MSRD) were determined relative to the lowest-temperature datum. The MSRD data were fit to predictions of the Einstein model [27], with the lowest-temperature MSRD being free to vary. Einstein temperatures so obtained were 377 K (+28 K, –26 K) for Al atoms in disordered \( \text{Fe}_3\text{Al}, 490 \) K (+74 K, –54 K) for Al atoms in ordered \( \text{Fe}_3\text{Al}, 391 \) K (+18 K, –15 K) for Fe atoms in disordered \( \text{Fe}_3\text{Al}, \) and 431 K (+40 K, –31 K) for Fe atoms in ordered \( \text{Fe}_3\text{Al}. \)

There was a strong reduction in the Al MSRD upon ordering, but a markedly smaller reduction in the Fe MSRD with ordering. The EXELFS measurements provide a relative displacement between Fe and Al atoms and their entire 1nn shell, which is a mixture of Fe and Al neighbors. Nevertheless, the backscattering cross section of Al is much smaller than that of Fe, so the EXELFS data are sensitive primarily to the relative displacements between the central atom and the Fe atoms in the 1nn shell. Using the expressions

\[
\Delta S^{\text{vib}}_{\text{Fe}} = 3k_b \ln \left( \frac{\theta_{\text{Fe}}^0}{\theta_{\text{Fe}}^1} \right) \\
\Delta S^{\text{vib}}_{\text{Al}} = 3k_b \ln \left( \frac{\theta_{\text{Al}}^0}{\theta_{\text{Al}}^1} \right)
\]

(20a,b)

where, for example, \( \theta_{\text{Fe}}^0 \) is the is the EXELFS-determined Einstein temperature for Fe in the ordered alloy, we find that and \( \Delta S^{\text{vib}}_{\text{Al}} = (0.81 \pm 0.41) \ \text{K}_\text{b} \ \text{atom}^{-1} \) and \( \Delta S^{\text{vib}}_{\text{Fe}} = 0.20 \pm 0.17 \ \text{K}_\text{b} \ \text{atom}^{-1} \). The EXELFS results indicate a big Al contribution to the entropy, even though the error is large. The \( \Delta S_{\text{Al}} = 0.37 \ \text{K}_\text{b} \ \text{atom}^{-1} \) deduced from the inelastic nuclear resonant x-ray scattering plus calorimetry is consistent with the \( \Delta S^{\text{vib}}_{\text{Al}} = (0.81 \pm 0.41) \ \text{K}_\text{b} \ \text{atom}^{-1} \) from the EXELFS. The error bars on the Fe EXELFS results, \( \Delta S^{\text{vib}}_{\text{Fe}} \), are so large that we cannot reliably extract any numerical value. These EXELFS data from Fe are clearly inadequate for determining the very small \( \Delta S^{\text{vib}}_{\text{Fe}} = \)
0.01 k\textsubscript{n} atom\textsuperscript{-1} measured by the inelastic nuclear resonant x-ray scattering, but are not inconsistent with it.

**Optical Modes**

We can make another independent estimate of $\Delta S_{\text{opt}}$\textsubscript{Fe}. We deduce the optical modes of the Al phonon partial DOS from the measured Fe phonon partial DOS, with guidance from a Born – von Kármán model of the lattice dynamics of ordered Fe\textsubscript{3}Al. From the lattice dynamics of D\textsubscript{0} ordered alloys we know that a total of 1/4 of the modes must be associated with the optical modes around 43 meV. This results from the fact that 3 out of 12 dispersion curves for the D\textsubscript{0} structure are associated with the optical modes [26]. We also know that 1/4 of the modes are associated with Al atoms, since 1/4 of the atoms in the alloy are Al. By integration of the experimental $g_{\text{Fe}}(e)$ of the ordered alloy, we find that a fraction of 0.08 of the intensity of the phonon partial DOS of $^{57}$Fe lies in the region of the optical modes around 43 meV. For the optical modes to account for 25\% of the total DOS, 76\% of the phonon partial DOS of Al atoms must therefore be associated with the optical modes. From the Born – von Kármán model of the ordered alloy (Fig. 6) we find a similar number of 80\% with the force constants of Robertson [26], and 70\% with the force constants of Krentzinger, et al. [28]. Most of the Al phonon partial DOS is associated with the optical modes.

We also know that for an ordered alloy, the energy ranges of the optical modes for the Al and Fe vibrations are identical. This is shown for the ordered alloy in the insert in Fig. 6, which also shows that the shapes of the phonon partial DOS curves for Fe and Al atoms are similar. Our experimental data show that with disorder, the optical modes shift downwards in energy, and some states appear in the gap. We make the assumption that the shapes of the phonon partial DOS curves of Fe and Al are the same, at least in the region of the optical modes. We tested if the change upon disordering of the optical modes, measured for Fe in Fig. 5, but scaled by the factor of 0.76/0.08 for Al, can account for the difference in vibrational entropy measured by calorimetry. The result of applying Eq. 7 to this synthesized Al phonon partial DOS is $\Delta S_{\text{opt}}$\textsubscript{Al} = 0.20 k\textsubscript{n} Al atom\textsuperscript{-1}, or 0.05 k\textsubscript{n} Al atom in the alloy. This is of the correct order to account for the change in vibrational entropy of the alloy upon disordering.

Again, it seems reasonable that the contribution of Fe atoms to the difference in vibrational entropy of order and disordered Fe\textsubscript{3}Al is small, and the main contribution is from Al atoms. Furthermore, it appears that much or most of this change in the Al phonon partial DOS originates with changes in the optical modes. It is interesting that theoretical calculations have not yet detected significant softening of the optical modes of disordered Ni\textsubscript{3}Al or disordered Fe\textsubscript{3}Al, but find instead a simple broadening of the modes [29-32], or even a stiffening of them [33].

**Atom Arrangements that Control the Phonon DOS**

The results of Fig. 5 are useful for determining the spatial range of chemical order that affects the phonon DOS. Two of the samples have chemical SRO, but only one has LRO. Figures 3 and 5 show that a substantial change in phonon partial DOS occurs when only a small amount of SRO is present in the alloy. For the three samples, their fractional differences in chemical SRO seem comparable to their fractional changes in $g_{\text{Fe}}(e)$. It is clear that the $^{57}$Fe phonon partial DOS in Fe\textsubscript{3}Al depends much more strongly on SRO than on LRO.

An analysis of why the chemical SRO should have an important effect on the vibrational entropy of the order-disorder transition was presented previously [10]. A general relationship between the phonon DOS and chemical short-range order may be expected from the slopes of phonon dispersion curves. Flat dispersion curves provide a high density of phonon states, especially when they include Brillouin zone boundaries. They also provide a slow group velocity of sound. Slow propagation of a wavepacket of energetic phonons requires that much of the
energy of lattice vibrations is associated with localized atom movements. We expect localized atom movements to be affected strongly by SRO. We should expect SRO to have a major effect on the phonon DOS because of the high density of phonon states associated with these localized atom movements. We note that this interpretation is at odds with interpretations of vibrational entropies of order-disorder transformations based on a Debye model with a constant velocity of sound.

SUMMARY

The phonon partial densities of states and the partial vibrational entropies of the different atoms in the unit cell were defined, and shown useful for elucidating reasons for differences in vibrational entropies of alloy phases. Inelastic nuclear resonant scattering spectra were measured on alloys of Fe,Al that were chemically disordered, partially-ordered, and D03-ordered. The relationship between the phonon partial DOS for 57Fe atoms and inelastic nuclear resonant x-ray spectra was explained, and used to extract phonon partial DOS spectra from the three alloys of Fe,Al. By comparison to previous calorimetry measurements, it is shown that the contribution of the Fe atoms to the vibrational entropy is an order of magnitude smaller than that of the Al atoms. This seems consistent with previous lower-quality EXELFS measurements on ordered and disordered Fe,Al. With the assistance of Born - von Kármán model calculations on the ordered alloy, it is argued that change in the vibrational entropy upon disordering originates primarily with changes in the dynamics of Al atom motions in the optical modes. The phonon DOS of 57Fe was found to change systematically with chemical short range order in the alloy. It was argued that changes in the vibrational entropy should originate primarily with changes in the chemical short-range order in the alloy, as opposed to long-range order.

ACKNOWLEDGMENTS

The work at Caltech was supported by the U. S. National Science Foundation under contract DMR–9816617, and the work at Argonne was supported by the U. S. Department of Energy under contract W–31–109–ENG–38.

REFERENCES