Partial phonon densities of states of ^{57}Fe in Fe-Cr: Analysis by a local-order cluster expansion

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Nuclear resonant inelastic x-ray scattering spectra were measured for ^{57}Fe in disordered body-centered-cubic alloys of Fe-Cr. Partial phonon density of states (DOS) curves were obtained from these data. These results, in conjunction with the results of Ruckert *et al.* [Hyperfine Interact. **126**, 363 (2000)] on Fe-Cr thin-film multilayers and alloys, were analyzed with a local-order cluster expansion method. Interaction partial phonon DOS functions for the different short-range correlation functions were obtained from the disordered alloys. These interaction DOS functions were used in reconstructing the ^{57}Fe partial DOS curves measured by Ruckert *et al.* on a set of thin-film multilayer samples of ^{57}Fe/^{56}Fe/Cr. The method worked well using terms up to a combined first- and second-nearest-neighbor triangle cluster, which were obtained reliably from the disordered alloys. The limitations of a basis set of correlation functions from disordered alloys are discussed but shown to be acceptable for the chemical trends of phonons in the Fe-Cr system.

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I. INTRODUCTION

In the past two decades, there has been considerable progress toward understanding the Gibbs free energies $G=H-TS$ of alloy phases and phase diagrams. Electronic structure calculations have proven powerful for assessing the enthalpy H, identifying thermodynamic ground states for $T=0$, and showing trends for materials under pressure at low temperatures. Static contributions to the entropy S are understood well, such as the configurational entropy of atom arrangements. Dynamical sources of entropy such as phonon entropy S_{ph} are known to be important,[1] but their systematics is less well understood, especially for disordered solid solutions.[2]

At modest temperatures, H and S for most alloy phases are determined primarily by their local arrangements of atoms, even when the bonding electrons are delocalized. A standard method to parametrize atom arrangements in crystalline alloys uses a hierarchy of local atom correlations, with contributions organized over an increasing number of atoms and an increasing range of distances. A cluster expansion is a systematic method for expressing a ground-state function of an alloy as a sum of terms, each being the product of an atomic correlation function for a specific localized cluster, and an interaction parameter to weight the importance of the cluster.[3–7] A set of atomic correlation functions $\{\xi_n\}$ is unique to each chemical arrangement $\vec{\sigma}$, whereas the set of interaction parameters $\{J_n\}$ is constant for alloys with the same lattice and specific volume. The cluster expansion method has proven efficient for evaluating the compositional dependence of the electronic energy and the configurational entropy of alloys because their interaction parameters decay quickly with the size of the cluster.[3,8,9] For phonon entropy, the formalism for the cluster expansion was developed and tested some time ago,[10,11] but it is not yet clear if the interaction parameters have the quick convergence that makes the cluster expansion method so useful as for other thermodynamic quantities. Physically, interatomic force constants are usually confined to short distances between atoms, but it is less well known if these force constants are sufficiently constant for alloys with different concentrations and local structures to allow reliable cluster expansions with relatively few terms. The systematic effects of bond stiffness versus bond length[2] suggest that short-range structural information may indeed be sufficient. A previous assessment showed that the phonon density of states (DOS) of Fe-Pt could be understood with the atomic arrangements of a first-nearest-neighbor shell of atoms, but this could involve many clusters.[12]

Obtaining cluster interactions often begins by calculating thermodynamic properties of different ordered structures. Ordered structures are well suited for band theoretical calculations and have well-defined atomic correlation functions that facilitate obtaining the effective cluster interactions by matrix inversion.[13] With these cluster interaction parameters, the more computationally challenging thermodynamic properties of disordered alloys are then obtained using the proper weighting of the correlation functions of the disordered alloys. On the other hand, although disordered solid solutions may be more challenging computationally, they often prove convenient experimentally when ordered structures are not available in nature. For disordered alloys, different atomic correlation functions can be emphasized by changing the alloy composition.

Although phonon entropy is a thermodynamic quantity amenable to analysis by cluster expansion methods, more information is contained in the phonon DOS, from which the phonon entropy can be readily calculated in the harmonic and quasiharmonic approximations. The phonon DOS is of interest in its own right because it gives insight into interatomic forces, and the DOS functions have considerable structure that is lost when the phonon entropy is obtained by averaging over all modes of vibration. In principle, a stan-

dard cluster expansion could be performed for each vibrational mode of the solid, each mode having its own set of interaction parameters. In what follows, however, we group the mode interaction parameters into functions that we call "interaction phonon DOS functions." In essence, we generalize the interaction parameters used in the cluster expansion method to be functions of phonon energy.

The Fe-Cr system was selected for experimental study in part owing to previous inelastic neutron-scattering studies of phonons in Fe-Cr alloys.[14–17] The present investigation used the technique of nuclear resonant inelastic x-ray scattering (NRIXS). This method gives the partial phonon DOS of ^{57}Fe atoms in the sample, i.e., the projection of the phonon DOS onto the motions of ^{57}Fe atoms. Our measurements were made on disordered body-centered-cubic (bcc) solid solutions of Fe-Cr, but the measurements were planned to complement previous measurements of the ^{57}Fe partial phonon DOS by Ruckert *et al.* on monolayers of ^{57}Fe in epitaxial FeCr multilayers.[18] The Fe-Cr disordered solid solutions and thin films have similar lattice parameters (bcc Fe and Cr have lattice parameters of 2.87 and 2.88 Å, respectively). This helps reduce volume effects, simplifying the interpretations of changes in the partial phonon DOS in terms of the local chemical order.

After explaining experimental details of the bcc ^{57}Fe-Cr samples and NRIXS measurements, we describe the practice of using the cluster expansion method with interaction functions for partial phonon DOS functions. The robustness of using interaction functions from disordered alloys is assessed in terms of the condition number for the matrix of correlation functions. These interaction functions, obtained from the present NRIXS data and measurements on bcc ^{57}Fe-Cr alloys by Ruckert *et al.*, are then used to reconstruct the partial phonon DOS functions from multilayered thin films.[18] The DOS functions of the multilayered samples are reproduced surprisingly well using clusters up to the triangle and up to second-nearest-neighbor distances from ^{57}Fe atoms. Short-range correlation functions can be obtained reliably from disordered Fe-Cr alloys and appear sufficient for understanding essential trends in the phonon entropy of Fe-Cr alloys.

II. EXPERIMENTAL METHODS

Alloys of $Fe_{1-x}Cr_x$ for $x_{Cr}=[0.70,0.47,0.30]$ were prepared by arc melting under an argon atmosphere using 99.99% Fe and 99.995% Cr. The alloys of composition $x_{Cr}=[0.47,0.30]$ were enriched to contain approximately 13 at. % of the ^{57}Fe isotope. The alloy of composition $Fe_{0.30}Cr_{0.70}$ was not enriched and therefore contained approximately 1 at. % of the ^{57}Fe isotope. There was negligible mass loss and minimal surface oxidation after melting, so the compositions are expected to be accurate to 0.1 at. %. The samples with $x_{Cr}=[0.47,0.30]$ were cold rolled to final thickness, sealed in a quartz tube under an argon atmosphere, and then annealed at 1100 °C for 72 h. The brittle ingot of $Fe_{0.30}Cr_{0.70}$ was sealed in a quartz tube under an argon atmosphere, annealed at 1100 °C for several hours, sectioned with a diamond saw, sanded to a thickness of 70 μm, and stress relieved at 400 °C. X-ray diffraction patterns were measured on all samples both before and after the heat treatments. The patterns showed diffraction peaks from only the bcc phase. There was no evidence of sigma phase or oxide.

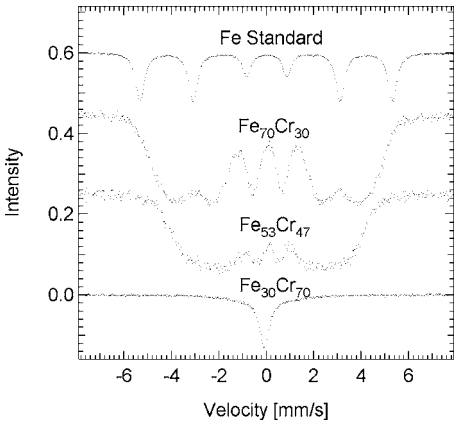

FIG. 1. Conventional room-temperature Mössbauer spectra of the alloys.

Transmission Mössbauer spectrometry was performed on all samples at room temperature with a conventional constant acceleration spectrometer, using a source of 75 mCi of ^{57}Co in Rh. Mössbauer spectrometry has been used extensively to characterize bcc Fe-Cr alloys and the sigma-phase compound.[17,19–23] The ^{57}Fe atom serves as a probe of its local environment, detecting the presence of Cr atoms in its first and second coordination spheres. The Mössbauer spectra of Fig. 1 are typical of those of disordered solid solutions.[20–23] The broadened magnetic sextets are expected for the high Cr concentrations in these alloys. No paramagnetic peak is detected in the center of the spectra from $Fe_{0.30}Cr_{0.70}$ or $Fe_{0.53}Cr_{0.47}$ that could indicate the presence of Fe in a Cr-rich regions caused by spinodal decomposition.[17] The high ^{57}Fe content in the two enriched samples contributes an unfortunate saturation distortion to the spectrum, however.

Nuclear resonant inelastic x-ray scattering[24–26] (NRIXS) was performed on all of the alloys at hutch 16-IDD at the Advanced Photon Source at the Argonne National Laboratory. Each sample was placed at a grazing angle to the incident photon beam. The incident photon energy was tuned to 14.413 keV, the nuclear resonance energy of ^{57}Fe. The delayed signal was measured from a single avalanche photodiode positioned 90° from the direction of the beam. Data were collected in scans of incident photon energy from −80 to +80 meV from the resonant energy, with a monochromator resolution of 2.2 meV. The $Fe_{0.30}Cr_{0.70}$, $Fe_{0.53}Cr_{0.47}$, and $Fe_{0.70}Cr_{0.30}$ samples were measured for 12, 5, and 17 h, respectively.

III. RESULTS AND DISCUSSION

A. Experimental results

The NRIXS spectra are shown in Fig. 2. The error bars are consistent with differences in ^{57}Fe enrichment and measuring times. The intense elastic peak at $E=0$ extends well off the figure. Nuclear scattering with phonon creation con-

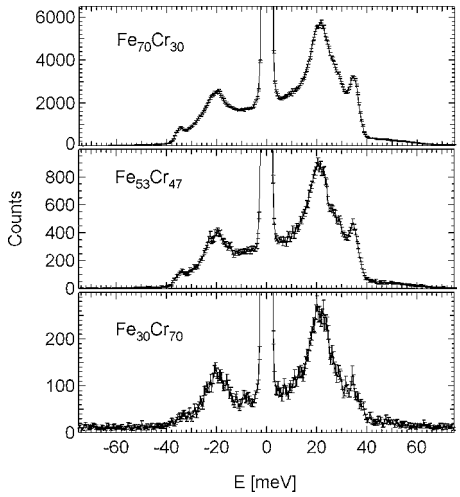

FIG. 2. Measured NRIXS spectra acquired from the three samples at room temperature.

tributes to the intensity to the right of the elastic peak; phonon annihilation processes contribute to the intensity at the left. The raw scattering data were summed and analyzed using the program PHOENIX,[27] which performs all of the calculations necessary to determine the ^{57}Fe partial phonon DOS, including removal of the elastic peak and multiphonon corrections. The ^{57}Fe partial phonon DOS curves for the three alloys measured in this experiment are shown in Fig. 3.

B. Local-order cluster expansion formalism

A general cluster expansion is useful for average thermodynamic quantities, but our experimental results are centered on ^{57}Fe atoms. An appropriate method for clusters localized around specific atoms is the "local-order cluster expansion,"[28] which is described first. A method applicable to both the local-order and general cluster expansions is then presented.

"Spin variables" σ are used for the two species of atoms, where an A atom (Fe) is assigned the factor $\sigma=+1$ and a B atom (Cr) has $\sigma=-1$. A cluster is a shape made by connecting a number of points, $n+1$, on the lattice. In the *local-order* cluster expansion, the clusters must contain the local point of interest l (e.g., an ^{57}Fe atom). The correlation function ξ_n is defined as the sum over all clusters of the products of the spin variables for each atom in the cluster:

$$\xi_n = \frac{1}{N_n}\sum_{\{p_i\}} \sigma_{p_1}\sigma_{p_2}\cdots\sigma_{p_n}. \tag{1}$$

Here, n also denotes the order of each term in the expansion. For example, $n=\{0,1,2\}$ for the point, pair, and triangle terms, respectively. In our local-order cluster expansion, $n=0$ is the point term because every point cluster is the atom of interest with $\sigma=+1$. The number of clusters of type n is N_n. The value of the spin variable at site p is σ_p, with each lattice point labeled from 1 to n.

It is straightforward to calculate the correlation functions ξ_n for a random solid solution of A and B atoms around a local point containing an A (Fe) atom. For the pair term, we perform the sum in Eq. (1) over the N_1 atoms in the vicinity of the local point,

$$\xi_1 = \frac{1}{N_1}\sum_{\{p_i\}} \sigma_{p_1},$$

$$\xi_1 = \frac{1}{N_1}(N_A\sigma_A + N_B\sigma_B),$$

$$\xi_1 = 1 - 2x_B. \tag{2}$$

Here N_A and N_B are the number of A and B atoms in the vicinity of the local point, $N_1=N_A+N_B$, $x_B=N_B/N_1$ is the concentration of species B, and $x_A=N_A/N_1=1-x_B$ is the concentration of species A. For a random solid solution, the probability of finding a particular atom on a site in any pair of atoms is again its concentration, so the triangle term ξ_2 is simply the product of the point correlation function with itself. Another factor of ξ_1 is used for ξ_3, and by induction

$$\xi_n = (1 - 2x_B)^n. \tag{3}$$

A function of the local atomic arrangement at a specified point, F^l, is a sum over the correlation functions multiplied by the corresponding interaction parameters $\{J_n^l\}$,

$$F_{m'}^l = \sum_{n=0}^{\nu-1} J_n^l \xi_{n,m'}. \tag{4}$$

Here m' is used to denote a specific atomic configuration on the parent lattice. This is often a specific ordered structure, but in the present work, it will be a disordered alloy of specified composition. The total number of terms used in the cluster expansion is ν. Often a set $\{F_m^l\}$ are known by calculations or direct measurements, and correlation functions $\xi_{n,m}$ are apparent from the configurations. The interaction parameters can then be obtained by inverting $\xi_{n,m}$ as follows:[13]

$$J_n^l = \sum_{m=0}^{\nu-1} F_m^l \xi_{n,m}^{-1}. \tag{5}$$

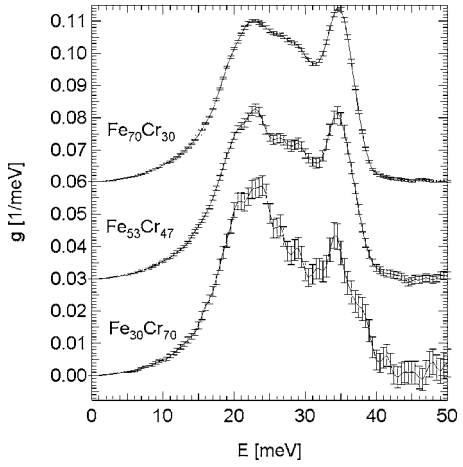

FIG. 3. ^{57}Fe partial phonon DOS curves for the three alloys measured with NRIXS.

The phonon entropy $S_{\mathrm{ph}}(E)$ for the specific alloy m' is, in the quasiharmonic approximation,[17]

$$S_{\mathrm{ph}}^{m'}(E) = 3k_B \int_0^E f^{\star}(E') g^{m'}(E') dE', \tag{6}$$

with

$$f^{\star}(E) \equiv [f_{BE}(E)+1]\ln(f_{BE}(E)+1) - f_{BE}(E)\ln(f_{BE}(E)), \tag{7}$$

where $f_{BE}(E)$ is the Bose-Einstein phonon occupancy factor and $g^{m'}(E)$ is the DOS for the particular alloy configuration m'. Both $f_{BE}(E)$ and $g^{m'}(E)$ are obtained at the same temperature. The partial phonon entropy is obtained from an equation of the same form, where now $g^{m'}(E)$ denotes the partial phonon DOS. Typically, the phonon entropy is not a function of energy, since the desired quantity is $S_{\mathrm{ph}}(E_c)$, where E_c is the upper limit of the phonon DOS. The upper limit on the integral can be taken to infinity because $g^{m'}(E)$ is zero for $E > E_c$.

Any ground-state thermodynamic quantity can be expressed with a cluster expansion.[5] This pertains to the partial vibrational entropy as it is obtained from the partial phonon DOS of ^{57}Fe atoms of Eq. (6),

$$3k_B \int_0^E f^{\star}(E') g^{m'}(E') dE' = \sum_{n=0}^{\nu-1} S_{\mathrm{ph},n}(E) \xi_{n,m'}, \tag{8}$$

where $S_{\mathrm{ph},n}(E)$ is equivalent to J_n of Eqs. (4) and (5). We have neglected the superscript l as the following formalism can be applied to both the local and general cluster expansions. By analogy to cluster interaction parameters, we call $S_{\mathrm{ph},n}(E)$ an "interaction phonon entropy." With independent phonons, consistent with harmonic or quasiharmonic theory, it is possible to evaluate a partial contribution to $S_{\mathrm{ph},n}$ from individual phonons, or from phonons within a small range of energy. Differentiating with respect to E gives the contribution from phonons within the energy range from E to $E+dE$,

$$g^{m'}(E) = \frac{1}{3k_B f^{\star}(E)} \sum_{n=0}^{\nu-1} \left[\frac{d}{dE} S_{\mathrm{ph},n}(E) \right] \xi_{n,m'}. \tag{9}$$

The similarity of Eq. (9) to Eq. (4) prompts the definition of an "interaction phonon DOS" $g_n(E)$,

$$g_n(E) = \frac{1}{3k_B f^{\star}(E)} \frac{d}{dE} S_{\mathrm{ph},n}(E), \tag{10}$$

so the phonon DOS from a specific configuration m' is

$$g^{m'}(E) = \sum_{n=0}^{\nu-1} g_n(E) \xi_{n,m'}, \tag{11}$$

which can be inverted formally in the same way as Eq. (5),

$$g_n(E) = \sum_{m=0}^{\nu-1} g^{m'}(E) \xi_{n,m'}^{-1}. \tag{12}$$

Equations (9) and (10) show the relationship between the interaction parameters $S_{\mathrm{ph},n}(E)$ and the interaction DOS functions $g_n(E)$. A cluster expansion of the DOS is done by performing a cluster expansion of the number of modes at each energy E.

If a useful cluster expansion can be performed with only a few terms, it is possible to overcome some difficulties associated with using correlation functions from disordered alloys. Equation (3) approaches zero as the number of terms n becomes large, but the most significant issue is the lack of unique information obtained from cluster functions with larger n—the correlation function basis becomes ill conditioned with an increasing number of terms. In practice, this means that although the fit to the thermodynamic functions may improve with n, the higher-order interaction parameters may not be determined reliably with experimental data on random solid solutions.

The condition of the $\xi_{n,m}$ matrix can be described in part by the absolute value of the determinant, which is the volume of the figure bounded by the vectors of the matrix. If a matrix is degenerate, e.g., if two of its vectors lie in the same direction, the volume of this figure will be zero, as its determinant. The other extreme is a matrix whose vectors span the space maximally. Here, the volume of this figure and the determinant are maximized.

An upper bound on the determinant of a $\nu \times \nu$ matrix with complex elements restricted to modulus M is known from the "Hadamard maximum determinant problem,"[29]

$$|\det A| = M^{\nu} \nu^{\nu/2}. \tag{13}$$

Our $\nu \times \nu$ matrix of correlation functions $\xi_{n,m}$ has all elements of modulus 1 or less [Eq. (3)]. A $(-1,1)$ matrix, a matrix whose elements lie on the unit sphere, can be constructed for $\xi_{n,m}$ only up to $\nu=2$, however. For $\nu > 2$, the maximum value of the determinant is

$$|\det A| = M^{\nu} 2^{-\nu} (\nu+1)^{(\nu+1)/2}, \tag{14}$$

where M is the largest modulus of the basis vectors. A matrix of correlation functions that satisfies Eq. (14) spans the space maximally. Our matrix composed of only correlation functions given by Eq. (3) is a Vandermonde matrix.[30] Its determinant is

$$|\det V| = \prod_{1 \le i < j \le \nu} (\xi_{1,j} - \xi_{1,i}), \tag{15}$$

which was maximized to find the set of alloys that provide an $\xi_{n,m}$ matrix that spans the space maximally. The results of this are given in Table I.

Using the determinant as a measure of the condition of the $\xi_{n,m}$ matrix simplifies the task of finding the best set of compositions for the disordered alloys. A better measure, however, is the matrix condition number κ,

TABLE I. Determination of most orthogonal basis using only alloys.

ν	$\{\xi$ basis$\}$	$\{x_{\mathrm{Cr}}\}$	$\lvert\mathrm{Det}\ V\rvert$	$2^{-\nu}(\nu+1)^{(\nu+1)/2}$	$\nu^{\nu/2}$
2	$\{-1,1\}$	$\{1,0\}$	2		2
3	$\{-1,0,1\}$	$\{1,1/2,0\}$	2	2	5.196
4	$\{-1,-1/\sqrt{5},1/\sqrt{5},1\}$	{1, 0.72, 0.28, 0}	1.1449	3.494	16
5	$\{-1,-\sqrt{3/7},0,\sqrt{3/7},1\}$	$\{1,0.83,1/2,0.17,0\}$	0.3665	6.75	55.90
6	$\{-1,-0.77,-0.29,0.29,0.77,1\}$	{1, 0.88, 0.64, 0.36, 0.12, 0}	0.0643	14.118	216
7	$\{-1,-0.83,-0.47,0,0.47,0.83,1\}$	$\{1,0.92,0.73,1/2,0.27,0.08,0\}$	0.0061	32	907.49

$$\kappa(V) = \|V\|_2 \|V^{-1}\|_2. \tag{16}$$

Here, the double brackets denote the matrix norm and the subscript denotes the use of the 2-norm. The condition number is a measure of the sensitivity of a matrix to numerical operations. A matrix with a condition number of 1 is perfectly conditioned, whereas an infinite condition number occurs when V is singular.[31] In our linear system, we take the matrix entries to have machine precision, which is the maximum possible relative error in representing a number as floating point. The interaction DOS vector does have an associated error, where error propagation from Eq. (12) yields

$$\delta_{g_n(E)} = \left[\sum_{m=0}^{\nu-1} (\delta_{g^{m'}(E)} \xi^{-1}_{n,m'})^2 \right]^{1/2}. \tag{17}$$

The value of κ/ν multiplied by the error bars on the measured alloy DOS provides the upper limit on the error bars for the interaction DOS functions. Table II shows the alloy compositions that were used in this experiment, along with the determinant and the ratio κ/ν of the corresponding $\xi_{n,m}$ matrix.

The interaction partial phonon DOS functions up to the triangle term, determined using the alloy sets in Table II, are shown in Fig. 4. These were calculated using Eq. (12). The interaction partial phonon DOS functions are shown for an increasing number of terms ν. The functions through the triangle interaction, $g_2(E)$, keep a consistent shape with increasing ν, although the triangle function has some change in shape for ν=5. The error bars increase in size as ν increases in a manner that is consistent with the ratio κ/ν given in Table II.

C. Application of local cluster expansion to thin films

Ruckert *et al.* prepared thin-film multilayer samples by molecular-beam epitaxy using layers of ^{56}Fe, ^{57}Fe, and Cr in different orders on the (001) plane, as shown in Fig. 5.[18]

TABLE II. Properties of alloy basis matrix.

ν	$\{x_{\mathrm{Cr}}\}$	$\lvert\det V\rvert$	κ/ν
2	{0.97, 0}	1.94	0.505
3	{0.97, 0.47, 0}	1.82	1.10
4	{0.97, 0.70, 0.30, 0}	0.94	1.87
5	{0.97, 0.70, 0.47, 0.30, 0}	0.14	6.97

Spectra from these samples give a unique opportunity for testing (1) if the cluster parameters obtained from disordered alloys are transferable to a very different type of chemical structure and (2) the range of effective cluster interactions that are needed for describing the phonon DOS in Fe-Cr. Only the partial phonon DOS of the ^{57}Fe atoms at the interface of the Fe and/or Cr layers was measured in the NRIXS experiments of Ruckert *et al.* For example, the thin-film sample FeCr1 depicted in Fig. 5 has the active layer of ^{57}Fe separated from the Cr layers by four layers of ^{56}Fe. The FeCr1 ^{57}Fe partial phonon DOS is almost identical to that of pure bcc Fe, showing that the local atomic environment information needed to describe its phonon properties is of shorter range than the distance to the Cr layer.

The correlation functions of the multilayers were determined using the ^{57}Fe local structure shown in Fig. 5. The first-nearest-neighbor (1NN) and second-nearest-neighbor

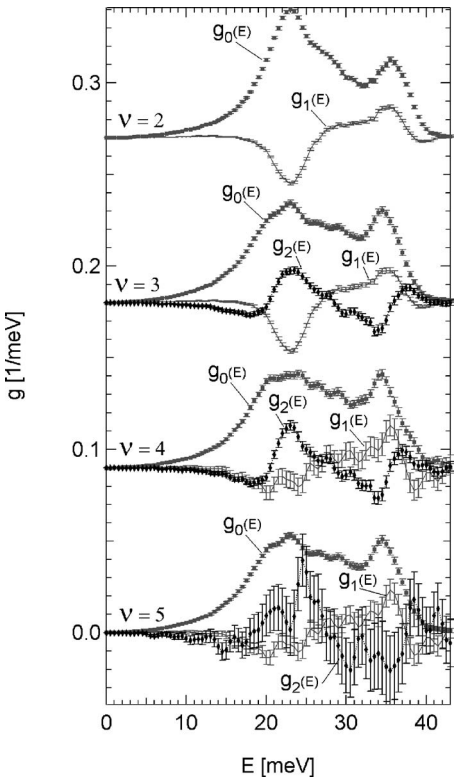

FIG. 4. Interaction partial phonon DOS functions from cluster expansions of the disordered alloys, showing changes with the number of terms.

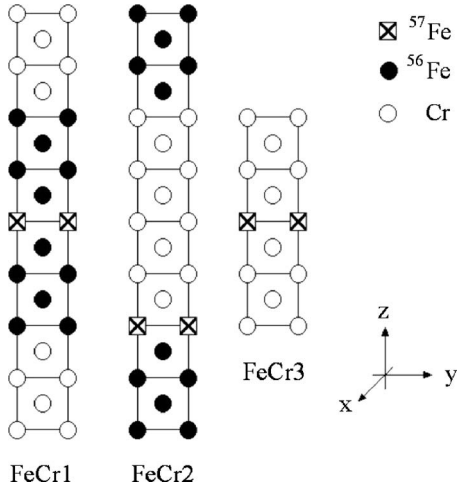

FIG. 5. Superstructure of thin-film samples. From left to right: FeCr1, FeCr2, and FeCr3. Empty circles are Cr, filled circles ^{56}Fe, and squares with an "x" inside are ^{57}Fe.

(2NN) distances are similar in the bcc structure, and therefore the 1NN and 2NN atoms were both used when determining the correlation functions of the pair and triangle terms. When determining the triangle term, only clusters containing at least one 1NN pair from the ^{57}Fe atom were included, because a cluster consisting of two 2NN pairs from the ^{57}Fe atom would also include a third-nearest-neighbor pair. The specific pair and triangle clusters used are shown in Fig. 6.

Figure 7 shows the ^{57}Fe partial DOS curves of the thin-film multilayers obtained using the interaction DOS functions from the disordered alloys (cf. Fig. 4) and the correlation functions given in Table III. Included in this table is the rms fit δ of the local-order cluster expansion to the measured ^{57}Fe partial DOS from literature. The correlation functions of the alloys measured in this experiment are also provided for comparison. The experimental ^{57}Fe partial phonon DOS curves vary significantly for the different Fe-Cr alloys and structures (Figs. 3 and 7), and the atomic structures of the

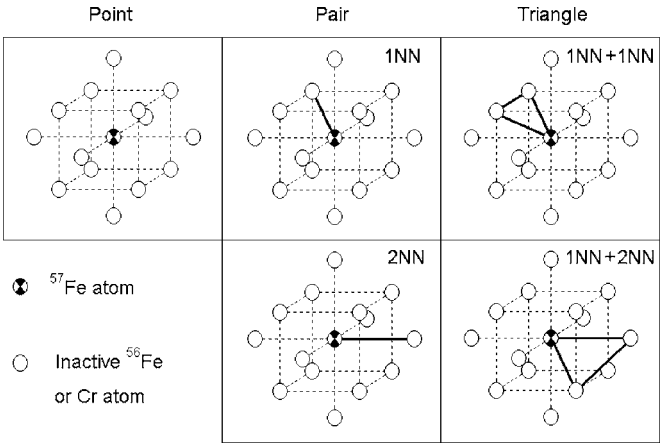

FIG. 6. Clusters used to describe the partial phonon DOS of the ^{57}Fe atoms at the interface of the thin-film multilayer samples. The 1NN and 2NN pair and triangle clusters are shown and are taken to be equivalent in the analysis.

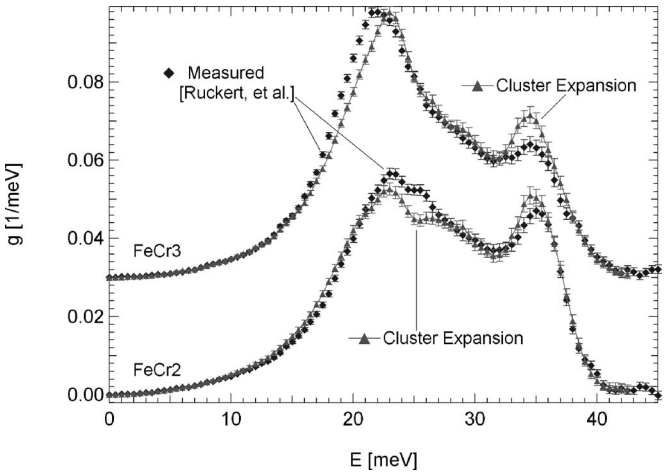

FIG. 7. Partial phonon DOS curves of the thin-film multilayers, and functions calculated from correlation functions from disordered alloys.

disordered solid solutions and the multilayer thin films are substantially different. We therefore consider the calculated curves in Fig. 7 to be remarkably successful.

It is evident from Table III that the local-order ^{57}Fe correlation functions of the FeCr3 multilayer and the $Fe_{0.30}Cr_{0.70}$ disordered solid solution are almost equal. Also, the correlation functions of the FeCr2 multilayer are both slightly greater than those of the $Fe_{0.53}Cr_{0.47}$ disordered solid solution. This provides an opportunity to test the cluster expansion without having to perform a matrix inversion. Figure 8 shows that the ^{57}Fe partial phonon DOSs are very similar for samples with similar correlation functions. This provides strong evidence that the DOSs are functions of the local chemical environment, as the thin-film multilayers and disordered alloys have quite dissimilar long-range order.

As a further test of the local-order cluster expansion, the correlation functions ξ_n for the FeCr2 and FeCr3 multilayer samples were found from the best least-squares fits to the partial phonon DOS functions of the FeCr2 and FeCr3 samples of Ruckert *et al.*, using the interaction functions of Fig. 4. The results, given in Table IV, show that the higher-order terms do not significantly affect the values of ξ_1 and ξ_2.

D. Local-Order effects in Fe-Cr

The contribution to the ^{57}Fe partial phonon DOS for each of the terms in the cluster expansion for $\nu=3$ using the alloys $x_{Cr}=\{0,0.47,0.97\}$ is shown explicitly in Fig. 4. Each of the

TABLE III. Correlation functions of thin films and alloys.

Sample	ξ_0	ξ_1	ξ_2	$\delta\times10^3$
FeCr2	1	2/7	1/3	3.29
FeCr3	1	−3/7	1/9	4.69
$Fe_{0.70}Cr_{0.30}$	1	0.4	0.16	
$Fe_{0.53}Cr_{0.47}$	1	0.06	0.0036	
$Fe_{0.30}Cr_{0.70}$	1	−0.4	0.16	

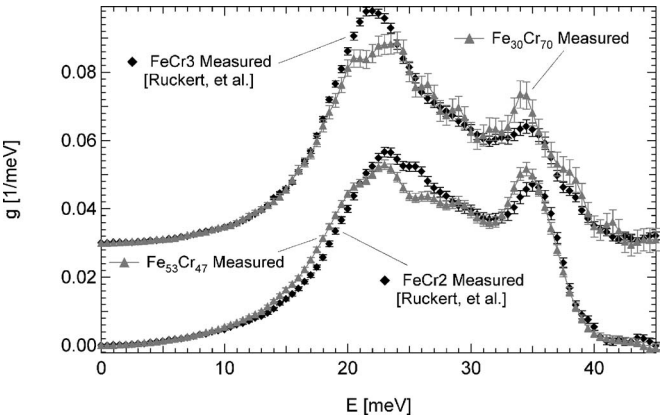

FIG. 8. Partial phonon DOS curves of the thin-film multilayers compared to the disordered solid solution with the most similar local-order ^{57}Fe correlation functions.

interaction partial phonon DOS functions can be interpreted as follows. The $n=0$ term is the ^{57}Fe partial phonon DOS of a random solid solution of $Fe_{0.50}Cr_{0.50}$. The $n=1$ term shows the effect on the partial phonon DOS of having different numbers of Fe and Cr atoms in the 1NN and 2NN shells of the ^{57}Fe atom. The triangle term, $n=2$, shows the effect of having like and unlike pairs of atoms within the 1NN and 2NN shells of the ^{57}Fe atom. The function $g_1(E)$ is added to the partial phonon DOS when the atom in the 1NN and 2NN shells of the ^{57}Fe atom is Fe and subtracted when it is Cr. The effect of Fe atoms in the 1NN and 2NN shells of the ^{57}Fe atom is therefore to decrease the number of low-energy modes and increase the number of high-energy modes, whereas Cr does the opposite. The function $g_2(E)$ is added when a pair in the 1NN or 2NN shell of the ^{57}Fe atom is composed of two of the same atoms. Like pairs increase the number of low-energy modes while decreasing the number of high-energy modes, whereas unlike pairs do the opposite. These statements about the effects of local atomic order on the partial phonon DOS were made possible by the cluster expansion analysis. For Fe-Cr, these are the largest effects of local atomic order on the partial phonon DOS.

The Fe-Cr system was well suited for identifying effects of local chemical order on phonons. We expect this method to work as well or better for fully ordered samples that are bcc and maintain the same lattice parameter for the different phases. In systems that are fully miscible in the bcc phase, such as CrV, perhaps only the DOS curves of the end members and the equiatomic alloy are needed to account for the main trends of the vibrational properties for all of the alloy concentrations.

TABLE IV. Correlation functions of thin films from alloy DOS.

Thin film	ν	$\delta\times 10^3$	ξ_1	ξ_2	ξ_3	ξ_4
FeCr2	3	2.16	0.259	0.559		
FeCr2	4	1.79	0.322	0.501	0.124	
FeCr2	5	1.74	0.350	0.533	0.140	0.400
FeCr3	3	3.65	−0.772	−0.174		
FeCr3	4	3.68	−0.682	0.025	−0.025	
FeCr3	5	3.29	−0.825	0.038	−0.475	0.075

IV. CONCLUSION

Partial phonon density of states (DOS) functions for ^{57}Fe atoms were measured by inelastic nuclear resonant scattering for disordered bcc Fe-Cr alloys. The local cluster expansion method was adapted to work with partial phonon DOS functions using interaction functions rather than interaction parameters. It was shown that disordered solid solutions can provide robust interaction functions for clusters as large as the combined first- and second-nearest-neighbor triangles, and these were obtained from the experimental data on disordered Fe-Cr alloys. The set of three pair and triangle clusters in the local cluster expansion was used to successfully reconstruct the ^{57}Fe partial phonon DOS functions measured by Ruckert *et al.* on Fe/Cr multilayers prepared by molecular-beam epitaxy. This success indicates that the interaction functions are transferable to different chemical arrangements of Fe and Cr on the bcc lattice, and the main trends in phonon entropy of the Fe-Cr system can be accounted for with relatively small clusters.

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