

Structure, electronic density of states and electric field gradients of icosahedral AlCuFe: An *ab initio* study of the original and a modified Cockayne model

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(Received 19 November 2003; published 30 March 2004)

We present a detailed analysis of electronic properties of the Cockayne model of icosahedral AlCuFe, both in its original form and after a structural relaxation using the *ab initio* density functional approach. The electronic density of states (DOS) and electric field gradients (EFG's) of the Al and Fe atoms in the original and the relaxed Cockayne models were calculated and compared with available photoemission, Mössbauer, and nuclear quadrupole resonance spectroscopy data. The relaxed and the original models show significantly different electronic properties. Both models are deficient in describing the available experimental data. The DOS's show two Fe-*d* peaks, where there is only one such peak in the photoemission spectroscopy data. These models also cannot account for the shape of the Mössbauer spectra. We show that the interchange between 12 Cu and 12 Fe atoms, each belonging to a single symmetry class, results in a smaller number of Cu-Fe nearest-neighbor pairs and a lowering of the total energy by an amount of $\Delta E \sim 50$ meV/atom. This "modified" version of the Cockayne model was further relaxed for the final comparison between the calculation and experimental results. The modified model shows a considerable improvement: The DOS has only one Fe-*d* peak, in agreement with photoemission spectroscopy data, and the calculated EFG's account very well for the experimental Mössbauer spectra.

DOI: 10.1103/PhysRevB.69.094206

PACS number(s): 71.23.Ft, 61.18.Fs

I. INTRODUCTION

Discovered¹ in 1987, icosahedral (*i*-)AlCuFe is one of the oldest thermodynamically stable quasicrystals (QC's). Its sharp diffraction spots, indicating a high degree of order,² and the availability of large single crystals³ have made it a popular alloy for studying electronic properties typical of stable icosahedral QC's.

Ab initio electronic structure calculations of *i*-AlCuFe have been performed by Trambly de Laissardière and Fujiwara,⁴ by Roche and Fujiwara⁵, and by Landauro^{6,7} and Solbrig.^{8,9} These calculations use the structural model of Cockayne and co-workers,¹⁰ which is based on a fit to x-ray-diffraction data and subsequent relaxation of the atom positions using pair potentials. The agreement of the above-mentioned calculations with experiments¹¹ is not fully satisfactory, indicating room for further improvement of the structural model of *i*-AlCuFe.

One way to further improve the Cockayne model is to use forces determined by *ab initio* density-functional calculations instead of forces based on empirical pair potentials to relax the atomic positions. In this paper we performed such an *ab initio* structural relaxation. We then calculated the electronic density of states (DOS) in the original and the relaxed Cockayne model, and compared it to photoemission spectroscopy (PES) results. We also calculated electric field gradients (EFG's) at the Al and Fe sites and compared them to Mössbauer and nuclear quadrupole resonance (NQR) spectroscopy results.

In Sec. IV we will show that the structural relaxation led to a significantly different DOS and significantly different

EFG's, indicating that it is important to perform such an *ab initio* structural relaxation in order to make accurate predictions for a given structural model. However, the relaxation did not lead to an improvement of the agreement between theory and experiment. Therefore, we investigated a second possibility to further improve the Cockayne model, namely, by interchanging atoms. In Sec. II we will explain which physical considerations we used to guide our search for favorable interchanges, and we will propose a modified model with interchanged Cu and Fe positions. In Sec. IV we will point out that we found a lower total energy for the modified model ($\Delta E = 50$ meV/atom), and we will show that the modified model gave significantly better predictions for available PES and Mössbauer spectroscopy data than the relaxed Cockayne model.

II. MODELS

A phase diagram of the Al-Cu-Fe system¹² shows a single icosahedral phase in a narrow composition range around Al₆₂Cu_{25.5}Fe_{12.5}, where the subscripts indicate atomic percentages. Nearby, there are high-order approximant phases and multiple-phase domains. A 1/1 approximant phase with roughly 135 atoms per unit cell forms, when 7 at% Al is substituted by Si.¹³

A structural model of *i*-AlCuFe (the Cockayne model or 1/1 Al_{62.5}Cu₂₅Fe_{12.5}) was published¹⁰ in 1993. It is a hypothetical 1/1 approximant with 128 atoms per unit cell. Its structure is based on x-ray-diffraction data¹⁴ from a sample with icosahedral symmetry.¹⁵ For the 1/1 approximant phase (1/1 AlCuFeSi) three structural models based on x-ray-diffraction data have been published.^{16–20} Their atomic coord-

TABLE I. Coordinates in units of the lattice parameter a of the original, the relaxed, and the modified Cockayne models. For the $4a$ sites $x = y = z$.

Model	Class	Site	$x(a)$	$y(a)$	$z(a)$
Original model	Al0	4a	0.451		
	Al1	12b	0.030	0.541	0.346
	Al2	12b	0.226	0.857	0.475
	Al3	12b	0.247	0.850	0.833
	Al4	12b	0.732	0.029	0.159
	Al5	4a	0.957		
	Al6	12b	0.732	0.343	0.336
	Al7	12b	0.230	0.533	0.635
	Cu0	4a	0.336		
	Cu1	12b	0.036	0.836	0.150
	Cu2	12b	0.554	0.022	0.858
	Cu3	4a	0.152		
	Fe0	4a	0.843		
	Fe1	12b	0.540	0.348	0.672
	Relaxed model	Al0	4a	0.461	
Al1		12b	0.026	0.544	0.336
Al2		12b	0.227	0.846	0.481
Al3		12b	0.235	0.848	0.835
Al4		12b	0.732	0.020	0.145
Al5		4a	0.957		
Al6		12b	0.718	0.345	0.340
Al7		12b	0.249	0.511	0.604
Cu0		4a	0.341		
Cu1		12b	0.039	0.851	0.147
Cu2		12b	0.541	0.032	0.852
Cu3		4a	0.154		
Fe0		4a	0.842		
Fe1		12b	0.538	0.342	0.668
Modified model		Al0	4a	0.462	
	Al1	12b	0.029	0.534	0.344
	Al2	12b	0.226	0.849	0.473
	Al3	12b	0.218	0.855	0.834
	Al4	12b	0.732	0.023	0.166
	Al5	4a	0.956		
	Al6	12b	0.724	0.347	0.333
	Al7	12b	0.251	0.498	0.582
	Cu0	4a	0.342		
	Cu1	12b	0.544	0.347	0.669
	Cu2	12b	0.544	0.033	0.847
	Cu3	4a	0.157		
	Fe0	4a	0.840		
	Fe1	12b	0.048	0.844	0.148

coordinates agree, but the decorations are different.²⁰ This complicates the study of these models. For that reason we limited ourselves to the Cockayne model.

We studied three models: (1) the Cockayne model as originally published,¹⁰ (2) the Cockayne model after an *ab initio* relaxation of the atomic positions (see Sec. III), and (3) the Cockayne model with interchanged Cu1 and Fe1 sites (see Table I), after a subsequent *ab initio* structural relax-

ation. We refer to the second model as the relaxed Cockayne model and to the third model as the modified Cockayne model. The atomic coordinates of these three models are given in Table I. The lattice parameter of the original Cockayne model is $a = 12.30 \text{ \AA}$. For the relaxed and the modified model $a = 12.22$ and 12.18 \AA , respectively.

In constructing the modified Cockayne model we made the following considerations. As mentioned in the Introduction (Sec. I), the Cockayne model is based on x-ray-diffraction data,¹⁰ which can be expected to give a good contrast between Al atoms on one side and Cu and Fe atoms on the other side. Therefore, only interchanges of Cu and Fe atoms can be expected to preserve the agreement of the original Cockayne model with x-ray-diffraction data. Further, as we will see in Sec. IV, the original (and relaxed) Cockayne model gave two Fe- d peaks in the electronic DOS, where PES (Ref. 11) shows only one such peak. In addition, the original (and relaxed) Cockayne model gave a Cu- d peak that is significantly narrower than the Cu- d peak in a PES spectrum¹¹ of *i*-AlCuFe. These comparisons suggested to us that the local environments of some of the Fe and Cu atoms in the original Cockayne model are unphysical. Extended x-ray absorption fine-structure studies^{21–24} indicate that the Fe atoms in *i*-AlCuFe are predominantly surrounded by Al atoms. We further anticipated that a higher number of Cu-Cu nearest-neighbor pairs would broaden the Cu- d peak in the DOS of *i*-AlCuFe. We therefore looked for interchanges of Cu and Fe atoms that would reduce the number of Fe-Cu nearest-neighbor pairs (and hence make the Fe environments more predominantly of Al character) and that would simultaneously increase the number of Cu-Cu nearest-neighbor pairs. It turned out that there is only one such interchange, namely, that of the atoms in the classes Cu1 and Fe1 (Table I).

Figure 1 illustrates some of the features of the modified Cockayne model. In particular, from Figs. 1(c) and 1(d) it is clear that each Fe1 atom has two neighboring Cu atoms and each Cu1 atom has one Fe and three Cu nearest neighbors. This is an improvement over the original Cockayne model, where each Fe1 atom has four neighboring Cu atoms, and each Cu1 atom has one Fe and one Cu nearest neighbor. From Figs. 1(c) and 1(d) it also follows that the number of Al nearest neighbors of the Fe1 atoms is greater in the modified Cockayne model (ten) than in the original model (nine). From Fig. 1(b) it is clear that atoms of the class Fe0 (Table I) are exclusively surrounded by Al atoms.

III. METHOD

We used several existing *ab initio* electronic structure computer programs. Here we briefly describe these programs and we provide details of our calculations.

The coordinates of the atoms of the original and the modified Cockayne models were relaxed with the Vienna *ab initio* simulation package (VASP).^{25,26} VASP performs a variational solution of the Kohn-Sham equations²⁷ in a plane-wave basis, using projector-augmented-wave potentials^{28,29} for describing the electron-ion interaction. The calculation of the Hellmann-Feynman forces acting on the atoms allows us to

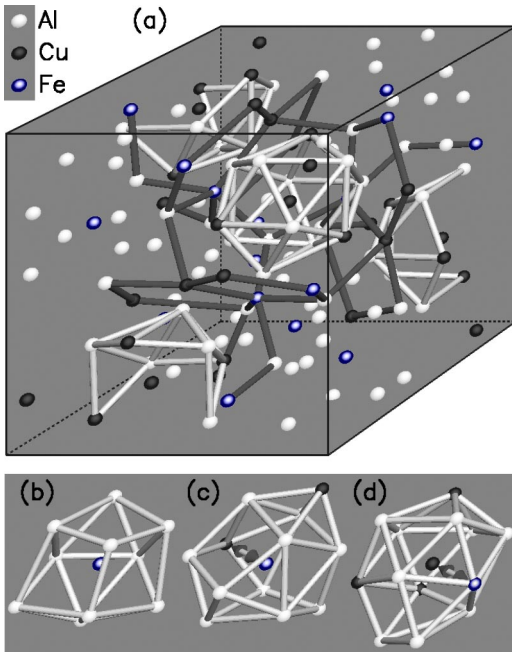


FIG. 1. (Color online) (a) Unit cell of the modified Cockayne model, consisting of four distorted icosahedra (light bonds) surrounding the Cu3 atoms (Table I) (Ref. 10). Four pentagonal dodecahedra (dark bonds) surround the icosahedra (Ref. 10). The subfigures show the nearest-neighbor environments of a (b) Fe0, (c) Fe1, and (d) Cu1 atom (Table I). Double arrows indicate Fe1 and Cu1 atoms that have been interchanged.

perform a full optimization of the atomic positions in the unit cell and of the lattice parameter. We also used VASP to compare the total energy of the relaxed and the modified Cockayne model.

In our VASP calculations we used the generalized gradient approximation³⁰ (GGA) for the exchange and correlation potential. The plane-wave cutoff energy was 273.2 eV. The eigenvalues at 4 inequivalent \mathbf{k} points, corresponding to 64 special \mathbf{k} points,³¹ were sampled³² with a smearing width³² of 0.2 eV.

Electronic DOS's were calculated with the linear muffin-tin orbital (LMTO) method in the atomic-sphere approximation (ASA).^{33,34} The LMTO-ASA method is a fast scheme for *ab initio* electronic structure calculations. It owes its speed to the relatively small basis set that it employs. Its accuracy is limited by the ASA.³⁵ Errors are small for close-packed systems, but may be large for open structures. Empty spheres can be placed in the interstitial volume between the atomic spheres to improve the close packedness of (the description of) a given structure.³⁵ Our procedure for finding empty spheres has been described in Ref. 36. One important parameter is the maximum of the overlap between any two spheres,³⁵ O , which provides a measure of how close packed a structure is. A value of $O \leq 0.16$ is acceptable.³⁴

In our LMTO47 calculations we used the local-density approximation³⁷ (LDA) for the exchange and correlation potential. For the modified Cockayne model we have checked that all features in the DOS were the same using the GGA.³⁰ We included 92 empty spheres per unit cell. This led to a

maximal overlap between the spheres of $O=0.147$ for the original, $O=0.164$ for the relaxed, and $O=0.162$ for the modified Cockayne model. For the original Cockayne model we performed an error analysis along the same lines as in Ref. 36. We estimated the resolution³⁶ to be 30 meV on the basis of a comparison with a calculation with 140 empty spheres ($O=0.140$). The resolution of our calculations for the relaxed and the modified Cockayne models should be slightly worse, since their structures are less close packed than that of the original Cockayne model. Our basis set consisted of s , p , and d states on the atoms and the empty spheres with a radius $r > 1 \text{ \AA}$, and s and p states on the empty spheres that were smaller. We calculated the DOS's as in Ref. 36.

EFG's were calculated with the linearized augmented plane-wave (LAPW) computer program WIEN97.³⁸ The LAPW method is an all-electron method. EFG's can be calculated without^{39,40} reference to empirical quantities such as Sternheim antishielding factors.

In our WIEN97 calculations we treated the Fe-3*p* semicore states as valence states using local orbitals⁴¹ to minimize linearization errors. The muffin-tin radii of the atoms ranged between 1.16 and 1.33 \AA . A typical number of plane waves was 6000. We used 15 inequivalent \mathbf{k} points. For the exchange and correlation potential we used the LDA.³⁷ We checked that our results were the same with fewer plane waves, fewer \mathbf{k} points, or using the GGA (Ref. 42) for exchange and correlation. The largest source of error in the EFG's is probably the uncertainty in the atomic positions. For the crystalline ω -Al₇Cu₂Fe phase we compared the EFG's for structures relaxed using LDA and GGA, respectively. GGA gave interatomic distances that were larger by just 0.6–2.3%. The EFG's differed by not more than $0.7 \times 10^{21} \text{ V m}^{-2}$.

IV. RESULTS

A. Electronic density of states

The DOS of the original Cockayne model is shown in Fig. 2(a). As mentioned in the Introduction (Sec. I) the electronic structure of the original Cockayne model has been calculated before.^{4–9} In these calculations^{4–9} the LMTO-ASA method is used. The results in Refs. 6–9 are most reliable, because they include the combined correction term,³³ which corrects for ASA-related errors. The calculations of Refs. 4 and 5 do not include this term. The necessity of including the combined correction has been discussed in Ref. 36. Our DOS [Fig. 2(a)] is close to the DOS of Refs. 6 and 9.

The main features in the DOS of the original Cockayne model are as follows. Near the band edge the DOS of the original Cockayne model stays close to the free-electron DOS [the dashed line in Fig. 2(a); it was fixed by requiring that the number of electrons between the band edge (at $E_F - 10.9 \text{ eV}$) and E_F equals the total number of s and p electrons (3 per Al, 1 per Cu, and 2 per Fe atom)]. Around $E_F - 4 \text{ eV}$ there is a broad peak due to Cu- d states.⁴³ The peaks at $E_F - 1.8 \text{ eV}$ and $E_F - 0.9 \text{ eV}$ are due to Fe- d states.⁴³ In contrast, in PES spectra^{11,44} of *i*-AlCuFe there is only one Fe- d peak at $E_F - 0.8 \text{ eV}$ (see Fig. 2). Another discrepancy

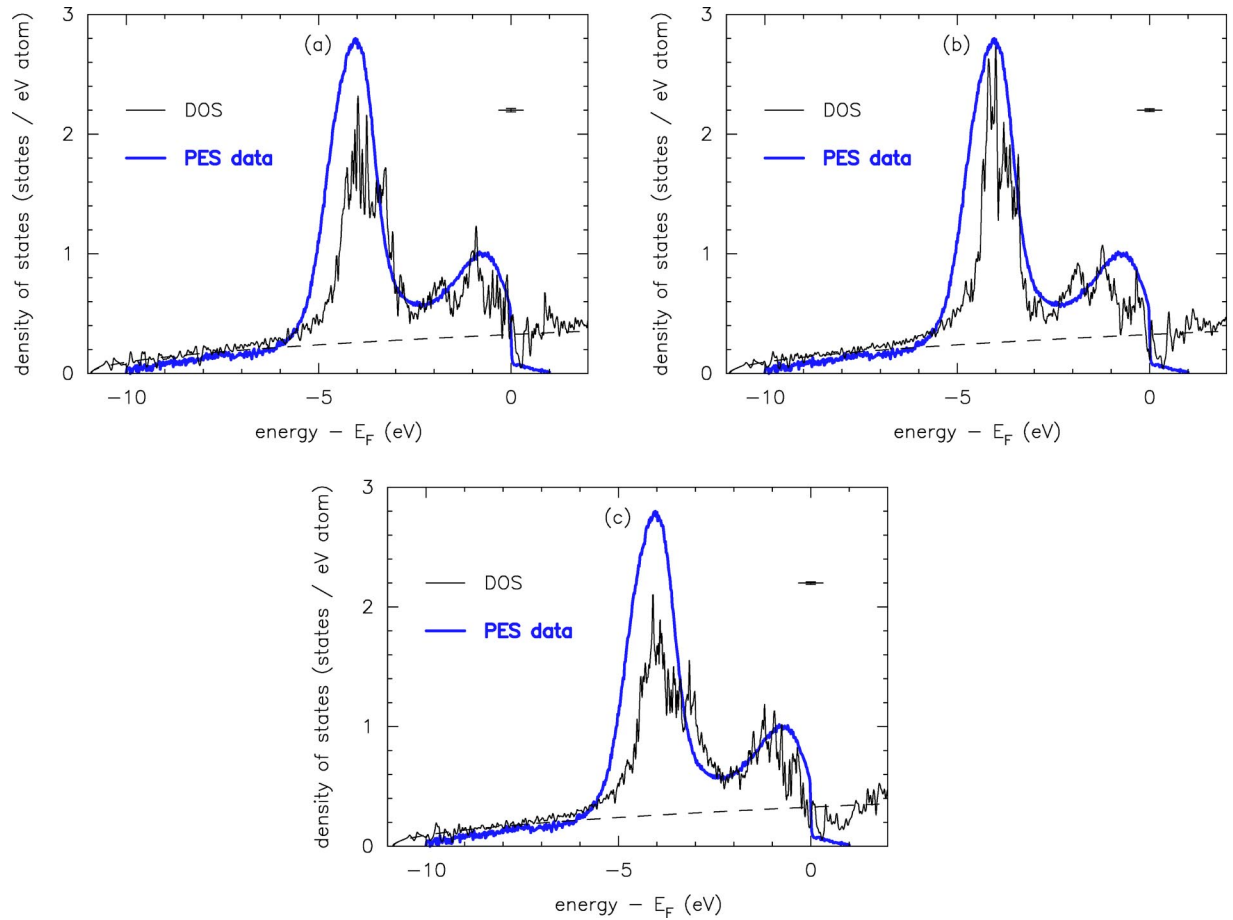


FIG. 2. (Color online) DOS of the (a) original, (b) relaxed, and (c) modified Cockayne models and a PES spectrum of $i\text{-Al}_{64}\text{Cu}_{24}\text{Fe}_{12}$ (Ref. 11). The DOS's were convoluted with a Gaussian with a full width at half maximum of 30 meV. Estimates of the maximum \mathbf{k} -space integration error are indicated. Dashed curves show the free-electron DOS (see text).

between the original Cockayne model and the PES spectra^{11,44} is that the calculated Cu- d peak is narrower than the Cu- d peak in the PES spectra.^{11,44}

The DOS of the relaxed Cockayne model is shown in Fig. 2(b). The Fe- d peaks are now at $E_F - 1.9$ eV and $E_F - 1.2$ eV. The Cu- d peak has become narrower than in the original Cockayne model. The differences between the DOS of the original Cockayne model [Fig. 2(a)] and the DOS of the relaxed Cockayne model [Fig. 2(b)] show that in order to accurately predict the DOS for a given structural model, it is important to use accurate atomic positions, which can be obtained through an *ab initio* structural relaxation. We have reached a similar conclusion in a recent *ab initio* study³⁶ of Al-Mn based icosahedral QC's. Figure 2(b) clearly shows that the relaxed Cockayne model cannot account for the PES spectrum^{11,44} of $i\text{-AlCuFe}$.

The DOS of the modified Cockayne model is shown in Fig. 2(c). There is only one Fe- d peak (around $E_F - 1.2$ eV). The Cu- d peak is now of similar width as the corresponding peak in the PES spectra^{11,44} of $i\text{-AlCuFe}$. Although we do not claim to have found a perfect agreement between our calculation for the modified Cockayne model and the PES spectra^{11,44} of $i\text{-AlCuFe}$, a comparison between Figs. 2(b) and 2(c) shows that the agreement of the modified

Cockayne model with the PES data is significantly better than that of the relaxed model.

Another indication that the modified Cockayne model is more realistic than the relaxed model was given by our result that the modified model has a lower total energy than the relaxed model ($\Delta E = 50$ meV/atom), which shows that the modified model is more stable than the relaxed Cockayne model. Several theoretical calculations at various levels of sophistication suggest a strong chemical short-range interaction between Fe and Al atoms in intermetallic alloys.^{45,46} Crystal structure data of various Fe and Al based intermetallics also bear evidence to this strong Fe-Al interaction.⁴⁷ Therefore, an increase in the number of nearest-neighbor Fe-Al pairs in the modified Cockayne model, combined with the reduction in Fe-Cu pairs, is responsible for the lowering of the total energy.

B. Electric field gradients

⁵⁷Fe Mössbauer and ²⁷Al NQR spectroscopy are sensitive to the local environments of the Fe and Al atoms in an alloy. These techniques can be used to distinguish between various structural models.⁴⁸ In this section we compare available experimental results with the theoretical results that we ob-

TABLE II. Calculated values of the EFG, the asymmetry parameter η , and the quadrupole splitting Δ of the Fe atoms in the Cockayne model.

Model	Class	Site	EFG (10^{21} V m $^{-2}$)	η	Δ (neV)
Original model	Fe0	4a	1.7	0	14
	Fe1	12b	1.8	0.7	16
Relaxed model	Fe0	4a	-0.5	0	4
	Fe1	12b	1.2	0.6	10
Modified model	Fe0	4a	-2.9	0	24
	Fe1	12b	-1.7	0.6	15
Experiment (Refs. 51–53)					18.1

tained for the Cockayne model. Theoretically, knowledge of the EFG's at the atomic sites suffices to predict the ^{57}Fe Mössbauer quadrupole splittings Δ as well as the ^{27}Al NQR spectrum of an alloy.

The ^{57}Fe quadrupole splitting is given by⁴⁸

$$\Delta = \left| \frac{1}{2} e^2 q Q \right| \sqrt{1 + \frac{\eta^2}{3}}, \quad (1)$$

where eq is the largest eigenvector of the EFG tensor (the term EFG is often used to denote eq), η is the asymmetry parameter of the EFG tensor, and Q is the nuclear quadrupole moment of ^{57}Fe . We used $Q = 16.0$ fm 2 , which is based on a systematic comparison of experimentally obtained quadrupole splittings and calculated EFG's,⁴⁹ and which has been confirmed by a nuclear shell-model calculation.⁵⁰ Experimentally,⁵¹ in $i\text{-AlCuFe}$ a wide distribution of quadrupole splittings Δ has been found, suggesting⁵² a continuous

distribution of local environments of the Fe atoms. The average quadrupole splitting⁵¹ in $i\text{-AlCuFe}$ is $\Delta = 18.1$ neV. This result has been confirmed for many icosahedral samples and high-order approximant phases.^{52,53} This shows that the local atomic and electronic structure of the Fe atoms in these samples is insensitive to the long-range order.⁵² Our calculated results for the Cockayne model are given in Table II. There is reasonable agreement between the quadrupole splittings Δ in the original Cockayne model and the experimental results. However, the structural relaxation changed the quadrupole splittings of the Fe atoms, leading to a much poorer agreement. The large difference between the quadrupole splittings Δ in the relaxed Cockayne model and in the $i\text{-AlCuFe}$ samples used in the experiments indicates that the Fe atoms in this model have different local environments than the Fe atoms in $i\text{-AlCuFe}$. The modified Cockayne model gives an average quadrupole splitting $\Delta = 17$ neV, in good agreement with the experimental value (Table II).

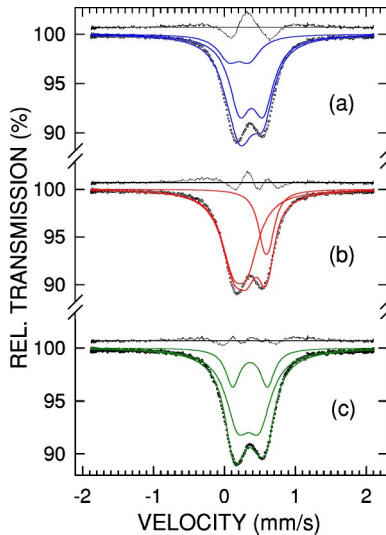


FIG. 3. (Color online) Comparison of the ^{57}Fe Mössbauer spectrum of $i\text{-Al}_{62.5}\text{Cu}_{24.5}\text{Fe}_{13}$ at 4.3 K (open circles) from Ref. 18 with the theoretical spectra (solid lines) generated for the values of Δ (Table II) calculated for the (a) original, (b) relaxed, and (c) modified Cockayne models. The component subspectra due to Fe at 4a and 12b sites are also shown. The zero-velocity scale in (a)–(c) is relative to $\alpha\text{-Fe}$ at room temperature. The differences between the experimental and theoretical spectra are shown above each spectrum.

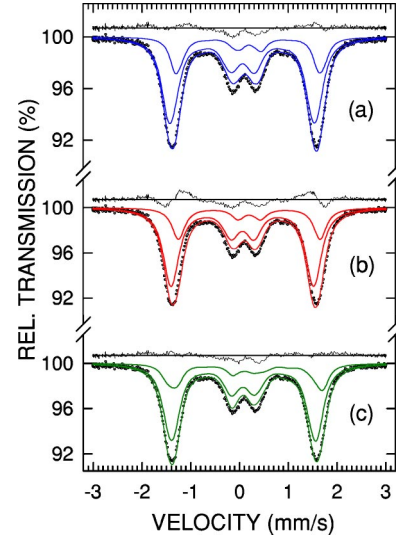


FIG. 4. (Color online) Comparison of the ^{57}Fe Mössbauer spectrum of $i\text{-Al}_{62.5}\text{Cu}_{24.5}\text{Fe}_{13}$ at 4.4 K measured in an external magnetic field of 9.0 T (open circles) from Ref. 18 with the theoretical spectra (solid lines) generated for the values of EFG and η (Table II) calculated for the (a) original, (b) relaxed, and (c) modified Cockayne models. The component subspectra due to Fe at 4a and 12b sites are also shown. The zero-velocity scale in (a)–(c) is relative to the $^{57}\text{Co}(\text{Rh})$ source at 4.4 K. The differences between the experimental and theoretical spectra are shown above each spectrum.

TABLE III. Calculated values of the EFG, the asymmetry parameter η , and the ^{27}Al NQR $5/2 \leftrightarrow 3/2$ transition frequency ν of the Al atoms in the Cockayne model.

Model	Class	Site	EFG (10^{21} V m^{-2})	η	ν (MHz)	
Original model	A10	4a	-3.2	0	3.4	
	A11	12b	1.3	1.0	1.3	
	A12	12b	-2.1	1.0	1.9	
	A13	12b	1.5	0.7	1.5	
	A14	12b	-2.4	0.8	2.4	
	A15	4a	-3.2	0	3.4	
	A16	12b	-3.5	0.6	3.4	
Relaxed model	A17	12b	-4.4	0.6	4.4	
	A10	4a	-2.8	0	2.9	
	A11	12b	1.2	0.7	1.2	
	A12	12b	1.7	0.8	1.6	
	A13	12b	-1.4	1.0	1.3	
	A14	12b	-3.4	0.5	3.4	
	A15	4a	-2.8	0	3.0	
Modified model	A16	12b	-4.5	0.5	4.6	
	A17	12b	-6.0	0.6	6.0	
	A10	4a	-2.2	0	2.4	
	A11	12b	-2.7	1.0	2.6	
	A12	12b	2.6	0.5	2.7	
	A13	12b	-2.3	0.6	2.3	
	A14	12b	-3.5	0.8	3.4	
Experiment (Refs. 56 and 58)	A15	4a	-3.2	0	3.4	
	A16	12b	-3.0	1.0	2.8	
	A17	12b	4.8	1.0	4.5	
						3.2 ^a -6.2

^aLowest frequency ν that could be measured in this experiment.

A direct comparison between the ^{57}Fe Mössbauer spectrum of $i\text{-Al}_{62.5}\text{Cu}_{24.5}\text{Fe}_{13}$ at 4.3 K measured in zero external magnetic field¹⁸ and the theoretical spectra generated for the values of Δ at the 4a and 12b Fe sites calculated for the original, the relaxed, and the modified Cockayne models (Table II) is shown in Fig. 3. The values of the center shift and of the full width at half maximum of the Lorentzian doublet subspectra corresponding to the 4a and 12b Fe sites were chosen in such a way as to get the best fit to the experimental spectrum. It is evident from this comparison that the spectra generated for the original [Fig. 3(a)] and the relaxed Cockayne model [Fig. 3(b)] cannot even account for the shape of the experimental spectrum, and that the spectrum generated for the modified model [Fig. 3(c)] accounts very well for the experimental spectrum.

Zero-field ^{57}Fe Mössbauer spectra of nonmagnetic powder materials provide information only on the absolute value of the EFG [Eq. (1)]. The sign of the EFG can be determined from ^{57}Fe Mössbauer spectra measured in external magnetic fields.^{48,54} Figure 4 presents a comparison between the ^{57}Fe Mössbauer spectrum of $i\text{-Al}_{62.5}\text{Cu}_{24.5}\text{Fe}_{13}$ at 4.4 K measured in an external magnetic field of 9.0 T (Ref. 18) and the spectra generated for the EFG and η values at the 4a and 12b Fe sites calculated for the original, the relaxed, and the modified Cockayne models (Table II). The Mössbauer spectra exhibiting mixed hyperfine magnetic dipole and electric quadru-

pole interactions must be treated using the exact Hamiltonian.^{48,54} If texture effects are negligible, one can assume that the principal axes of the EFG tensor are randomly oriented with respect to the external magnetic field. The algorithm for calculating the spectra in such a case is given by Blaes and co-workers⁵⁵ and was used here. The values of the center shift and of the full width at half maximum of the subspectra corresponding to the 4a and 12b Fe sites were chosen in such a way as to get the best fit to the experimental spectrum. The comparison in Fig. 4 shows that the spectra generated for the modified Cockayne model fit best the in-field spectrum.

The ^{27}Al NQR $\pm \frac{3}{2} \leftrightarrow \pm \frac{5}{2}$ transition frequency ν is given by⁵⁶

$$\frac{6e^2qQ}{20h}f(\eta), \quad (2)$$

where $Q = 14.66 \text{ fm}^2$ is the nuclear quadrupole moment⁵⁷ of ^{27}Al and $f(\eta)$ is a smoothly varying function of the asymmetry parameter η (see Ref. 56). The ^{27}Al NQR $\pm \frac{3}{2} \leftrightarrow \pm \frac{5}{2}$ transition has been measured^{56,58} in $i\text{-AlCuFe}$, showing a wide distribution of frequencies ν between 3.2 and 6.2 MHz. Unfortunately, this experiment^{56,58} was insensitive to frequencies below 3.2 MHz. Our calculated results are listed in Table III. The differences between the original and the re-

laxed Cockayne models show again that in order to make accurate predictions for a given structural model, it is important to use accurate atomic positions. For the relaxed and the modified models we found a wide distribution of frequencies ranging from 1.5 to 6.0 and 2.3 to 4.5 MHz, respectively, in qualitative agreement with the NQR experiments. Considering the uncertainties in the experiment a quantitative comparison between our calculated values and experiment is not meaningful.

V. CONCLUSION

In this work we have proposed a modified version of the Cockayne model of *i*-AlCuFe. The electronic properties of this model are in much better agreement with the available experimental data on *i*-AlCuFe than those of the original model. The modified model differs minimally from the Cockayne model in that it involves interchanging a class of 12 Cu atoms with 12 Fe atoms. The original Cockayne model was proposed in 1993 on the basis of x-ray diffraction data. The interchange of Fe and Cu positions that we proposed in this work is not expected to affect the x-ray-diffraction pattern significantly. We have shown that the total energy of the modified model is lower than that of the original model, indicating that the new atomic configuration is energetically more favorable than the original one. In particular, we argued that a greater number of Fe-Al combined

with a smaller number of Fe-Cu nearest-neighbor pairs is responsible for the lowering of the total energy.

One of the most apparent failures of the original Cockayne model to account for available experimental results is that it predicts that there are two Fe-*d* peaks in the electronic DOS, where only one such peak has been found in PES experiments. We have shown that our results for the modified Cockayne model agree significantly better with the PES results. In particular, we found that in the modified model there is only one Fe-*d* peak. A detailed comparison of the calculated EFG's for our models with zero-field Mössbauer spectroscopy data and Mössbauer spectroscopy data obtained in a magnetic field of 9.0 T showed again that the modified model gives superior predictions.

Finally, it is worth mentioning, that throughout this paper we have compared theoretical results for a hypothetical approximant (the Cockayne model) with experiments that have been performed on QC's. Ideally, one should use as large an approximant as possible for a comparison with real QC's.

ACKNOWLEDGMENTS

Financial support for this work was provided by the Natural Sciences and Engineering Research Council of Canada. The LMTO calculations were performed on computers of SHARCNET (Hamilton, Canada).

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