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Phys. Rev. B **96**, 100201 — Published 20 September 2017

DOI: [10.1103/PhysRevB.96.100201](https://doi.org/10.1103/PhysRevB.96.100201)

Anomalous random correlations of force constants on the lattice dynamical properties of disordered Au-Fe alloys

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Au-Fe alloys are of immense interest due to their biocompatibility, anomalous hall conductivity, and applications in various medical treatment. However, irrespective of the method of preparation, they often exhibit a high-level of disorder, with properties sensitive to the thermal or magnetic annealing temperatures. We calculate lattice dynamical properties of $\text{Au}_{1-x}\text{Fe}_x$ alloys using density functional theory methods, where, being a multisite property, reliable interatomic force constant (IFC) calculations in disordered alloys remain a challenge. We follow a two fold approach: (1) an accurate IFC calculation in an environment with nominally zero chemical pair correlations to mimic the homogeneously disordered alloy; and (2) a configurational averaging for the desired phonon properties (*e.g.*, dispersion, density of states, and entropy). We find an anomalous change in the IFC's and phonon dispersion (split bands) near $x=0.19$, which is attributed to the local stiffening of the Au-Au bonds when Au is in the vicinity of Fe. Other results based on mechanical and thermophysical properties reflect a similar anomaly: Phonon entropy, *e.g.*, becomes negative below $x=0.19$, suggesting a tendency for chemical unmixing, reflecting the onset of miscibility gap in the phase diagram. Our results match fairly well with reported data, wherever available.

PACS numbers: 62.20.-x, 63.50.Gh, 65.40.-b, 65.20.dk

Gold (Au) and iron (Fe) and their alloys continue to attract attention. Due to the higher magnetic state of Fe in Au-Fe than in pure Fe, various properties have been studied, including thickness dependent spin-glass behavior and anomalous hall conductivity in Fe/Au multilayers.[1–5] Due to its exceptional biocompatibility and favorable physical properties, Au-Fe nanoparticles find various applications in medical sciences.[6–10] Gold-rich Au-Fe alloys form a face-centered-cubic (fcc) structure. Although fcc is a high-temperature phase, Au-Fe alloys up to 53 at.%Fe are reported to be easily stabilized at room temperature.[11–14] Due to sensitivity of magnetic and chemical properties to annealing temperatures, these alloys require at most care in their synthesis, especially as disorder is quite common and difficult to control. Hence, chemical disorder plays an important role in their anomalous structural and magnetic properties.

For alloys to have useful applications, mechanical stability is a necessary criteria. Studying the lattice dynamics provides direct stability information and gives idea about local atomic environment, and related phenomena. Experimentally, techniques like nuclear resonant inelastic X-ray Scattering (NRIXS), inelastic neutron scattering (INS), and Mossbauer spectrometry are used to investigate the elementary excitation in disordered alloys.[14, 15] But, to date, there is no singularly accepted *ab initio* theoretical approach available to address lattice dynamics in disordered alloys, mainly due to configurational averaging and the associated computational cost. In fact, the challenge is to address the off-diagonal disorder arising out of the force constant matrix between two sites. In addition, the sum rule obeyed by the force constants implicitly makes the disorder at a

site dependent upon its neighborhood, *i.e.*, environmental disorder.

Historically, various approximate models are proposed to address disorder. The Virtual Crystal Approximation (VCA)[16] and Coherent Potential Approximation (CPA) are two widely known single-site examples, which also suffer from deficiencies.[17–21] VCA, the simplest among many, involves simple compositional averages of the constituent potentials and completely ignores environmental effect. The single-site CPA suffers from capturing the multisite effects expected in lattice dynamics, such as, off-diagonal and environmental disorder. Some generalization to the CPA, *e.g.*, Itinerant CPA (ICPA)[21], Dynamical Cluster Approximation (DCA)[22], and its first-principles version (*i.e.*, non-local CPA (NL-CPA)[19, 20]), address two-site disorder. These methods consist of various promising features, but they are usually limited to specific types of off-diagonal disorder or to small clusters due to computational expense. The Special Quasirandom Structure (SQS) technique[23] is being utilized more often to estimate environmental effects of disorder. It involves a fully-ordered cell (useful for band-structure method) in a layered arrangement of atoms that nominally exhibits zero chemical pair correlations (within a specified range of neighbor 2 – 3 shells) and mimics those of the homogeneously disordered alloy. To predict the lattice dynamical properties of disordered systems, accurate calculation of force constants as well as an appropriate configurational average over the disorder environment are equally important.

Here, we combine two techniques to correctly address the above issues: the SQS and Augmented Space Recursion (ASR). ASR is a powerful method to capture multi-

x	1.00	0.50	0.25	0.19	0.06	0.00	Direction
Au-Au		26.39	21.79	19.05	16.66	17.52	110_{xx}
Fe-Fe	9.29	14.08	9.16	2.39	9.38		110_{xx}
Au-Fe		13.89	10.98	10.98	9.20		110_{xx}
Au-Au		30.57	26.18	23.06	20.33	21.03	110_{xy}
Fe-Fe	17.88	14.48	1.49	2.92	10.67		110_{xy}
Au-Fe		16.78	12.05	13.20	10.85		110_{xy}
Au-Au		-6.37	-6.95	-6.64	-6.52	-5.94	110_{zz}
Fe-Fe	8.15	2.68	-8.01	-2.35	-1.60		110_{zz}
Au-Fe		-1.62	-2.86	-3.17	-2.84		110_{zz}

TABLE I. Force constants (N/m) for $\text{Au}_{1-x}\text{Fe}_x$ along $[110]$. The measured data for pure Au ($x = 0$) are 16.63, 20.82, -8.62 along 110_{xx} , 110_{xy} , 110_{zz} directions respectively.[14].

site disorder effects, as required in the phonon problem. A detailed description of the ASR formalism for phonons is given in supplementary material (section S1).[24] For a given size and symmetry cell, the SQS is used in conjunction with the small displacement method[25] to calculate the estimated force constants in a disordered alloy. ASR then performs the configurational averaging, with these disordered force constants. We calculated the phonon dispersion, density of states, lifetime, vibrational entropy, and thermo-mechanical properties for the $\text{Au}_{1-x}\text{Fe}_x$.

Spin-polarized, density functional theory (DFT)[26] calculations are performed with a projected augmented wave (PAW)[27] basis using the local density approximation (LDA), as implemented in the Vienna Ab-initio Simulation Package (VASP).[28, 29] We chose an optimal 32-atom SQS unit cell[30] to perform all the calculations for $\text{Au}_{1-x}\text{Fe}_x$ for $x = 0.50, 0.25, 0.19$ and 0.06 , providing good accuracy. For SQS structure of a given alloy, all the atoms were relaxed to achieve energy (force) convergence of up to 10^{-6} eV (10^{-3} eV/Å). We use a high-energy cutoff of 450 eV, with a Monkhorst-Pack $6 \times 6 \times 6$ k-mesh grid.[31] For $x = 0.50, 0.25, 0.19$ and 0.06 , respectively, optimized lattice parameters in $\text{Au}_{1-x}\text{Fe}_x$ were 3.83, 3.96, 4.00, and 4.05 Å. The experimental lattice parameter for $x = 0.50, 0.30, 0.20$ and 0.03 are 3.908, 3.991, 4.026 and 4.072 respectively, which compared fairly well with theory. Phonons were calculated using the small displacement method as implemented in PHON,[25] and the atomic force fields were obtained using 48, 96, 96 and 19 displacements for the respective x 's. For elastic constants, we used *PBEsol* exchange-correlation functional[32] with a $10 \times 10 \times 10$ Γ -centered k-mesh for total-energy calculation at different strains.

As SQS provides structures with reduced symmetry (not fcc), the force constant matrix become random and asymmetric, which cannot be used directly in ASR for configurational averaging. To extract meaningful parameters for the proper fcc symmetry, a directional aver-

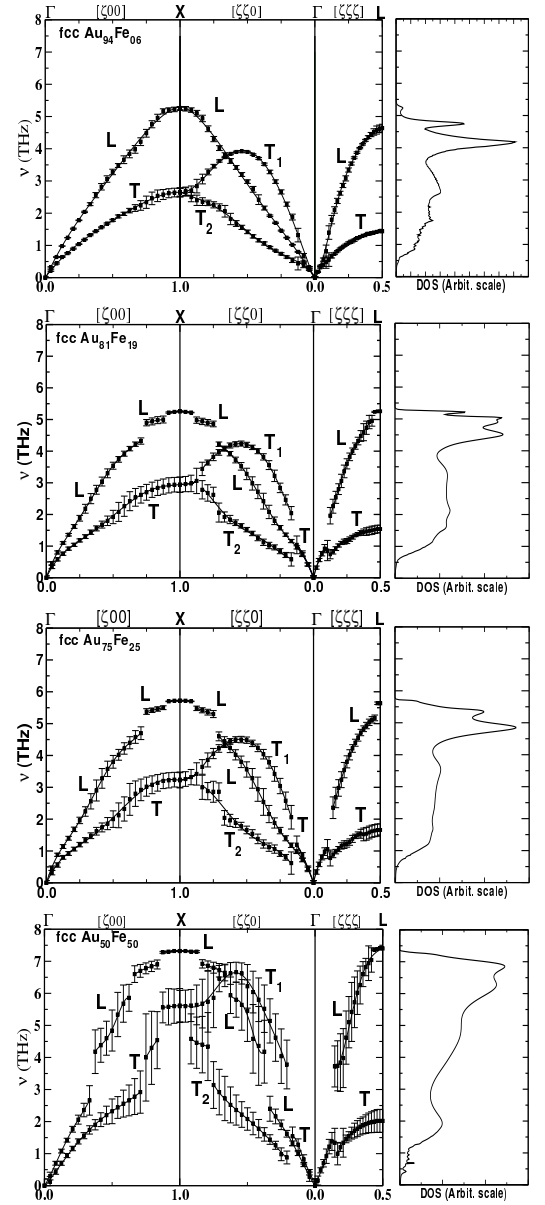


FIG. 1. (Left) Using force constants from 32-atom SQS, phonon dispersion for $\text{Au}_{1-x}\text{Fe}_x$ along high-symmetry $[\zeta 00]$, $[\zeta \zeta 0]$, $[\zeta \zeta \zeta]$, where $\zeta = |\vec{k}|/|\vec{k}_{max}|$ for reciprocal-space vector \vec{k} . Longitudinal (L) and transverse (T) modes are indicated. Bars indicate the calculated full width at half maxima (FWHM). (Right) Projected Density of States (DOS).

age mapping method is adopted. For fcc symmetry, we mapped all 12 nearest neighbor matrix elements for Au-Au, Fe-Fe and Au-Fe pairs in $\text{Au}_{1-x}\text{Fe}_x$ at each site along $[110]$ using $\phi^{101} = T^\dagger \phi^{110} T$, where T is the transformation matrix along different directions.

The averaged force constants for all pairs are tabulated in Table I. Notably, Au-Fe force constants become stiffer as we increase the iron concentration (%Fe). Addition of Fe in pure Au makes the Au-Au pair more stiff but Fe-Fe either becomes softer or remains unaf-

Parameters	Pure Au	Au ₉₄ Fe ₀₆	Au ₈₁ Fe ₁₉	Au ₇₅ Fe ₂₅	Au ₅₀ Fe ₅₀	Pure Fe
C_{11} (GPa)	196.09 (201.63) ^a	192.22	222.01	205.04	211.29	328.35 (243.1) ^c
C_{12} (GPa)	164.14 (169.67) ^a	161.38	180.94	159.24	153.41	164.56 (138.1) ^c
C_{44} (GPa)	44.57 (45.44) ^a	48.69	57.64	61.53	81.75	136.00 (121.9) ^c
B (GPa)	174.79 (180.32)	171.66	194.63	174.51	172.70	219.16 (173.1)
G_V (GPa)	33.13 (33.65)	35.38	42.80	46.08	60.61	114.36 (94.1)
G_R (GPa)	25.97 (26.15)	26.13	33.46	36.74	47.26	107.57 (79.74)
$G_H = \mu$ (GPa)	29.55 (29.90)	30.76	38.13	41.41	53.94	110.96 (86.94)
Y (GPa)	83.93 (85.01)	87.07	107.37	115.12	146.56	284.82 (223.41)
C' (GPa)	15.98 (15.98)	15.42	20.53 (20.7) ^b	22.90	28.93	81.90 (52.50)
C_p (GPa)	119.56 (124.22)	112.69	123.30	97.71	71.66	28.56 (16.18)
ν	0.42 (0.42)	0.42	0.41	0.39	0.36	0.28 (0.28)
K_ζ	0.89 (0.89)	0.89	0.87	0.84	0.81	0.63 (0.68)
A^Z	2.79 (2.84)	3.16	2.81	2.69	2.82	1.66 (2.32)
P	5.92 (6.03)	5.58	5.10	4.21	3.20	1.98 (1.99)
λ (GPa)	155.09 (160.38)	151.15	169.21	146.90	136.74	145.18 (115.14)
v_l (m/s)	3335.20 (3377.67)	3372.61	3735.33	3675.10	4079.53	6523.11 (6058.51)
v_t (m/s)	1238.84 (1244.67)	1282.61	1472.16	1560.33	1915.67	3586.33 (3322.86)
Θ_D (K)	162.87 (162.4 \pm 2) ^d	169.44	196.73	209.35	264.61	539.29 (472.7 \pm 6) ^d

TABLE II. Calculated parameters for Au, Fe and four alloys. Parenthetic values are measured data.^a[33], ^b[34], ^c[35], ^d[36]

fect. Interestingly, Au₈₁Fe₁₉ shows a turning point, where the force constant matrix elements exhibits a non-monotonous change. This anomaly is also reflected in the phonon dispersion, entropy, and other properties. The origin of this cannot be explained simply by the changes in lattice parameters or the overall electron DOS at the Fermi energy (E_F). Below we provide a deeper explanation.

Au-Fe alloys are known for their rich magnetic properties.[11, 37] Pure Fe in its stable bcc phase has a magnetic moment of 2.13 μ_B /atom, in agreement with previous theoretical and experimental data.[38, 39] As %Fe decreases from 0.50 to 0.06, the Fe moments increases from 2.71 to 2.99 μ_B /atom, also found previously.[14, 40] fcc Au is a non-magnetic metal. However, we found that the Au 5d moments are 0.083 (0.146) in Au₇₅Fe₂₅ (Au₅₀Fe₅₀), similar to other reported theory and experimental values of 0.099 (0.197), respectively.[11] (detailed result can be found in supplementary [24] section S2.)

Figure 1 shows phonon dispersions for Au_{1-x}Fe_x along high-symmetry directions. Notice the split band behavior with $x \geq 19\%$. Such splittings normally arise for systems with dominant mass or force constant disorder. Ni-Pt is a classic example of such behavior. In their elemental phase, Pt-Pt force constants are 55%

larger than Ni-Ni. Although the force constant difference here is not that significant, the mass difference is higher ($M_{Au}/M_{Fe} = 3.53$). Such splitting is a consequence of strong resonance, arising mainly out of dominant mass disorder here. Near resonances the FWHM become very large, as is clear in Fig. 1. ASR is expected to correctly address both mass and force constant disorders, mainly in the higher frequency region, as demonstrated in our earlier papers.[41, 42] Figure 1 also shows the phonon DOS, where the higher (lower) frequency region is dominated by Fe (Au), as expected by mass. It also explains the increase in number of states in the higher frequency region as the %Fe increases. Our calculated phonon-dispersion and DOS compares fairly well with previous experimental data.[14] The anomalous band splitting arises for $x \geq 0.19$, the turning point in the force constants (Table I). This behavior can be understood from the evolving nature of Au-Au bond in an Fe-matrix. When Fe is substituted in Au, there are two types of force constants that Au-Au pairs acquire. The pairs that do not contain Fe in their vicinity has force-constants similar to that of pure Au. However, pairs that exist in the neighborhood of Fe increasingly stiffen as %Fe increase, which causes an increase in the energy of some Au-modes above the cut-off energy of Au-modes and hence causes the splitting. This behavior can be

explicitly found in thermo-mechanical properties of the alloy, as seen below.

For a material, thermo-mechanical parameters are directly related to the second-order elastic constants. For a cubic crystal, there are three independent elastic constants denoted by C_{11} , C_{12} , and C_{44} . Here we use a strain-energy approach[30, 43] to evaluate C_{ij} at various %Fe, along with bulk modulus (B), shear modulus (G_V , G_R , G_H), Young's modulus (Y), shear constant (C'), Cauchy pressure (C_P), Poisson's ratio (ν), Kleinman parameter (K_ζ), Zener's anisotropy ratio (A^Z), Pugh's indicator (P), Lames's co-efficients (λ and μ), longitudinal and transverse sound wave velocity (v_l and v_t), Debye temperature (Θ_D), high-temperature limit to the thermal conductivity, as obtained via Clarke's model (κ_{min}^{Clarke})[44] and Cahill's model (κ_{min}^{Cahill}) [45]. All the properties help assess the mechanical stability of the material (see supplementary material[24] (section S3. and S4.) for details).

Table II presents the calculated values of these quantities along with available experimental data. Our data (C_{ij} 's) agrees within 2–5% of the experiment for Au[33]. For pure Fe, calculated C_{11} is overestimated by 25% while C_{12} and C_{44} by 19% and 11% compared to experiment, respectively. This is due, as well-known, to the GGA exchange-correlation function used here, which tends to underestimate the lattice constants for 3d transition metals.[46, 47] The Born-Huang's mechanical stability criteria[48] ($C_{11} - C_{12} > 0$, $C_{11} + 2C_{12} > 0$ and $C_{44} > 0$) are satisfied for both the elements and alloys. The calculated $C' = 20.5$ GPa for $\text{Au}_{81}\text{Fe}_{19}$ compares well with that measured 20.7 GPa.[34] All our calculated results are expected to be within 10-15% of the measured values, and will be interesting to be verified experimentally.

Pure Au has high B but small G_H , which makes it very ductile, as seen by its Pugh's indicator (5.92),[49] where materials with $P > 1.75$ are ductile. With increasing %Fe, the size and coupling force mismatch makes the system more stiffer (see Table I) resulting in reduced ductility and higher Young's modulus. $C_p > 0$ [50] suggests metallic bonding character, as well as higher conductivity. High ν values confirm this. $A^Z > 1$ [51] for both the elements and alloys points to highly anisotropic deformation in the material (higher possibility of micro-cracks). K_ζ [52] (between 0 and 1) indicates the nature of bonding. A lower (higher) K_ζ indicates dominant bond bending (stretching), as found here for Au-Fe. Lame's constant λ suggests large incompressibility of these alloys. Debye temperature (Θ_D) increases with disorder, attributed to higher mass fluctuation and increase in frequency of thermal vibrational modes.

At $x=0.19$, a similar anomaly (as in force constants and phonon dispersion) is encountered in some elastic properties (e.g., C_{11} , C_{22} , B, and C_P), reflecting the dominant force constant disorder and the emergence of resonance mode in the dispersion. Such unusual behavior is also

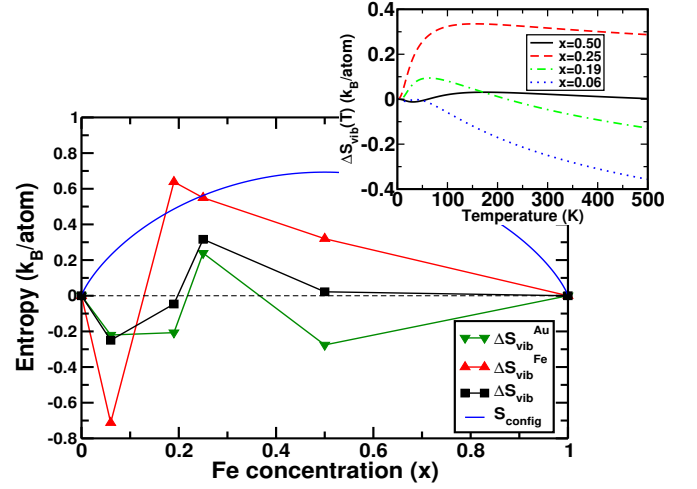


FIG. 2. (Color online) Excess phonon entropy vs. x for $\text{Au}_{1-x}\text{Fe}_x$ at $T = 300$ K and configurational entropy of mixing S_{config} (blue curve). Inset shows ΔS_{vib} vs. T at various x .

predicted by Munoz et al. at $x=0.2$, which are attributed to the increasing stiffness of Au-Au bonds with increasing %Fe, and primarily a local effect.

Next, we have calculated the temperature dependence of excess vibrational entropy, $\Delta S_{vib} = (1-x)\Delta S_{vib}^{Au} + x\Delta S_{vib}^{Fe}$, where ΔS_{vib}^{Au} (ΔS_{vib}^{Fe}) are the partial contribution to vibrational entropy from Au (Fe) respectively at each x . These are calculated as, $\Delta S_{vib}^M = S_{vib}^M(alloy) - S_{vib}^M(pure)$, [$M = \text{Au}, \text{Fe}$]. $S_{vib}^M(alloy)$ is estimated using the partial phonon density of states for respective elements at a given x . $S_{vib}^M(pure)$ is vibrational entropy of pure element in its respective equilibrium phase. Configurational entropy of mixing can be expressed as, $S_{config}(x) = -k_B[x\ln(x) + (1-x)\ln(1-x)]$. Figure 2 shows the concentration dependence of excess phonon entropy for $\text{Au}_{1-x}\text{Fe}_x$ at 300 K and configurational entropy of mixing. Square and triangle up (down) symbols indicate the total and partial vibrational entropies for Fe (Au). The inset shows the temperature dependence of excess vibrational entropy at various Fe concentrations. Clearly $x=0.19$ is an anomalous point which separates the two unique region of phase diagram. In other words, phonon entropy of mixing is negative for Fe concentrations $\leq 19\%$, beyond which it becomes positive. If we compare the configurational entropy of mixing, the calculated phonon entropy at $x=0.06$ Fe is much larger and negative in sign. This implies that, upto 19% Fe, configurational entropy supports chemical mixing, but phonon entropy favours unmixing, predicting miscibility gap in the alloy phase diagram.[53] Such discontinuity in the excess phonon entropy is attributed to the sudden up-rise of ΔS_{vib}^{Au} at $x=0.25$, which arises due to the stiffening of Au-Au bonds in the vicinity of the Fe atoms. One can also explain this behaviour from the enhancement of disorder broadening (see Fig. 1), a known fact

for entropy enhancement. A similar abrupt change in excess entropy is also seen in the temperature dependence of ΔS_{vib} at $x = 0.19$ (see inset). Our calculated phonon entropy agrees fairly well with similar measured data published elsewhere [14]. Small discrepancies can be attributed to under estimation of phonon DOS in experimental neutron weighted measurements.

In conclusion, we employ a new first-principles approach combining the Special Quasirandom Structures (SQS) and Augmented Space Recursion (ASR) formalism to study the lattice dynamical and thermo-physical properties of fcc $\text{Au}_{1-x}\text{Fe}_x$ alloys. This system is interesting because of the large difference in their constituent masses, force constants and scattering lengths. In addition Fe, unlike in its elemental state, acquire larger magnetic moment in the alloy. We found that, as the Fe concentration increases, the force constants tends to stiffen in the disordered environment. Above $x = 0.19$, phonon dispersion shows a split band behaviour suggesting strong that often arise due to dominant mass and/or force constant disorder. The anomaly at $x = 0.19$ is better described from our calculated phonon entropy which suggests the possibility of chemical unmixing below 19% Fe and hence the onset of miscibility gap in the phase diagram. Such anomaly is also reflected in some of our calculated mechanical properties as well. As % Fe increases, size enhancement and force constants mismatch stiffens the material which accounts for the increased Young's modulus and lower ductility. From materials perspective, $\text{Au}_{1-x}\text{Fe}_x$ alloy is predicted to be mechanically stable, very ductile but highly anisotropic (possibility of micro-cracks are high). One of the main ideas of this paper is to establish the combined SQS + ASR approach as an efficient and accurate method to study the lattice dynamical properties for random alloys.

ACKNOWLEDGEMENT

AA acknowledges DST-SERB (SB/FTP/PS-153/2013) for funding to support this research. JK acknowledges financial support from IIT Bombay in the form of TA-ship. DDJ was funded by the U.S. DOE, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division. Ames Laboratory is operated for the U.S. DOE by Iowa State University under contract DE-AC02-07CH11358.

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