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First-principles theory of the temperature and compositional dependence of atomic short-range order in disordered Cu-Pd alloys

R. V. Chepulskii*
Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom
and Department of Solid State Theory, Institute for Metal Physics, N.A.S.U., Kyiv-142, UA-03680, Ukraine

J. B. Staunton
Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom

Ezio Bruno and B. Ginatempo
Dipartimento di Fisica and Unità INFM, Università di Messina, Salita Sperone 31, 98166 Messina, Italy

D. D. Johnson
Department of Materials Science and Engineering, University of Illinois, Urbana, Illinois 61801

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We combine the first-principles, Korringa-Kohn-Rostoker coherent potential approximation based calculations of compositional fluctuations with a statistical mechanical ring approximation to study the temperature (T) and composition (c) dependence of the atomic short-range order (SRO) in disordered, face-centred cubic, Cu-Pd alloys. The fourfold splitting of SRO peaks around the equivalent $X(0,1,0)$ points in reciprocal space is obtained in a wide T-c region. Such splitting is shown to be an ''energy'' effect caused by the absolute minima of the Fourier transform of the effective atomic interactions and related previously to the existence of nested sheets of the disordered alloy's Fermi surface. However, we find that the T dependence of the SRO peak position is mostly an ''entropy'' effect. Both the calculated T and c dependences of the SRO peaks position are in good correspondence with the experimental data. The real-space effective atomic interactions and SRO parameters indicate the tendency for longer-period structures with increasing Pd concentration, as observed.

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I. INTRODUCTION

Diffuse scattering and atomic short-range order (SRO) in disordered fcc $\mathrm{Cu}_{1-c}\mathrm{Pd}_c$ alloys around the concentration $c=0.25$ have been subjected to intensive experimental and theoretical study. Experimentally,[1–10] it has been observed that the fourfold splitting of the diffuse scattering intensity (related to the SRO Fourier transform peaks[11]) at the X points (0,1,0) and equivalent positions in reciprocal space (see Fig. 1) takes place over a wide range of temperatures and concentrations. The size of the splitting is both temperature and concentration dependent. In particular, at thermal equilibrium, this magnitude increases with temperature and/or concentration.

In Ref. 12, the atomic interaction parameters for the disordered fcc Cu-Pd alloys were extracted from experimental SRO data corresponding to one particular temperature and concentration, using the analytical α-expansion method of Refs. 13 and 14 to describe the statistical mechanics of concentration fluctuations. Then, by use of these fixed parameters, the fourfold splitting of the SRO Fourier transform was investigated for a number of temperatures and concentrations. As a result, an increase of the size of the splitting with temperature was obtained in agreement with experiment. However, in contradiction with more recent experimental data,[10] the temperature dependence was found to grow with concentration.

In Refs. 15–17, a local density approximation (LDA) derived first-principles electronic structure theory of the splitting phenomena in $\mathrm{Cu}_3\mathrm{Pd}$ was developed. This theory is based on the mixed-space cluster expansion fitted to LDA full-potential total energies of ordered compounds. From the calculations, a temperature dependence of the splitting was obtained which compared well with experimental data. However, a narrow temperature interval was considered and the compositional dependence of the splitting was not studied at all.

In Ref. 18, a first principles concentration-wave approach based on a finite-temperature, electronic density functional,

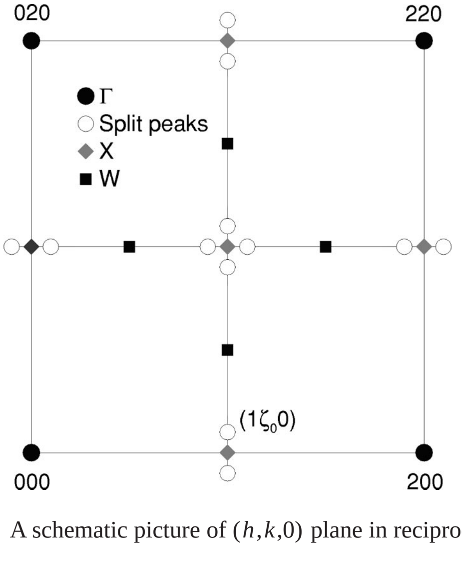

FIG. 1. A schematic picture of $(h,k,0)$ plane in reciprocal space.

mean-field grand potential of a random alloy was used to investigate the SRO of Cu-Pd alloy for a number of concentrations. The electronic structure calculations were carried out with the Korringa-Kohn-Rostoker coherent potential approximation (KKR-CPA) methodology[18] (see also Ref. 19) and electronic state filling including Fermi-surface effects were focused upon. Good agreement with the experimentally measured size of the splitting of the SRO peaks about the X points was obtained and this was linked naturally to the nesting of flat, parallel sheets of alloy Fermi surface. This feature has recently been measured by two-dimensional angular correlation of annihilation radiation (2D-ACAR) experiments.[20] However, not all electronic effects on an ideal fcc lattice were considered in Ref. 18. This was done in a later paper[21] but for $\mathrm{Cu}_{1-c}\mathrm{Pd}_c$ alloy only at one concentration $c=0.25$. Another shortcoming of both studies[18,21] is the use of a mean-field-like spherical model approximation for the compositional fluctuations that leads to the temperature dependence of the splitting being missed.

In this paper, we study the SRO in disordered Cu-Pd alloys by use of the same KKR-CPA concentration wave approach as in Ref. 21 (see also Ref. 22) but in a wide concentrational interval. To describe the temperature dependence of the splitting, we use an accurate and simple analytical ring approximation developed by one of us and co-workers.[23–29] This approximation has been shown to be able to describe the temperature dependence of the positions of SRO peaks for simpler models even with constant atomic interactions[30–32] (in contrast to the widely used Krivoglaz-Clapp-Moss[33–35] and spherical model[13,21,24,25,36–40] approximations). Within the ring approximation, it is possible to take into account the long-range contributions to the atomic interactions without major complications (in contrast to the cluster-variation[41] and Monte Carlo[42] methods), because it is the lattice Fourier transform of the effective atomic interactions which appears in the formalism. Moreover, it has been shown[26,31] that the numerical accuracy of this approximation improves with an increase of the effective range of the atomic interactions.

This reliance that the ring approximation makes directly on the Fourier transform of the SRO parameters means that there is no need to neglect parameters from coordination shells with large radii. This is important for the description of such a sensitive effect as splitting of the SRO peaks in wave-vector space about a symmetry point because it requires a large number of SRO parameters in direct space.[7,12,15] The advantage of the ring approximation compared to the analytical γ-expansion[13] and α-expansion[14] methods is that (at the same or higher numerical accuracy[26,28,43]) we have to solve only one simple nonlinear integral equation [see below Eq. (11)] instead of the complicated system of equations as in the γ-expansion method.[43]

We note that our approach used in the present paper (a joint implementation of KKR-CPA linear-response and ring approximations) may be considered as complimentary to that used in Refs. 15–17. So, besides the comparatively more extended investigation performed in the present paper, it is also important to study the same issues as in Refs. 15–17 for comparison of the advantages and shortcomings of both approaches.

II. CONFIGURATIONAL DESCRIPTION

Any binary alloy configuration may be represented as $C_{\mathbf{R}}=1$ (or 0) if the site $\mathbf{R}$ *is (is not)* occupied by an A-type atom. Using this in the framework of the lattice gas model,[44] a general Hamiltonian H of a two-component A-B disordered alloy with a Bravais crystal lattice can be written in the following form:

$$H=\Phi^{(0)}+\sum_{\mathbf{R}_1}\Phi^{(1)}_{\mathbf{R}_1}(C_{\mathbf{R}_1}-c)+\frac{1}{2}\sum_{\mathbf{R}_1,\mathbf{R}_2}\Phi^{(2)}_{\mathbf{R}_1,\mathbf{R}_2}(C_{\mathbf{R}_1}-c)\times(C_{\mathbf{R}_2}-c)+\frac{1}{6}\sum_{\mathbf{R}_1,\mathbf{R}_2}\Phi^{(3)}_{\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3}(C_{\mathbf{R}_1}-c)(C_{\mathbf{R}_2}-c)\times(C_{\mathbf{R}_3}-c)+\cdots, \tag{1}$$

where $\Phi^{(n)}_{\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_n}$ $(n=1,2,\ldots)$ are the series expansion coefficients,

$$c=\langle C_{\mathbf{R}}\rangle=N_{\mathrm{A}}/N, \tag{2}$$

the sign $\langle\cdots\rangle$ means the statistical average, and c and N_{A} are the concentration and total number of A-type atoms in the alloy, correspondingly; the summations on the real-space lattice vectors $\mathbf{R}_i$ $(i=1,2,\ldots,N)$ are carried over all N crystal lattice sites.

In this work, we investigate the behavior of the Warren-Cowley[45,46] SRO parameters $\alpha_{\mathbf{R}}$:

$$\alpha_{\mathbf{R}_1-\mathbf{R}_2}=(\langle C_{\mathbf{R}_1}C_{\mathbf{R}_2}\rangle-c^2)[c(1-c)]^{-1}. \tag{3}$$

In fact, $\alpha_{\mathbf{R}}$ is a normalized pair correlation function. The positive or negative values of $\alpha_{\mathbf{R}}$ correspond, respectively, to the correlated attraction or repulsion of A-type atoms separated by the vector $\mathbf{R}$. Besides, we study the behavior of the Fourier transform $\alpha_{\mathbf{k}}$ of the SRO parameters $\alpha_{\mathbf{R}}$:

$$\alpha_{\mathbf{k}}=\sum_{\mathbf{R}}\alpha_{\mathbf{R}}\exp(-i\mathbf{kR}),$$

$$\alpha_{\mathbf{R}}=N^{-1}\sum_{\mathbf{q}}\alpha_{\mathbf{q}}\exp(i\mathbf{qR}). \tag{4}$$

In Eqs. (4) and below, the summation on $\mathbf{q}$ is carried over all N points specified by the cyclic boundary conditions in the corresponding first Brillouin zone.

To calculate the SRO, we use the analytical ring approximation[23–29] developed by use of the thermodynamic fluctuation method.[34,35,41,47,48] Here a modified thermodynamic perturbation theory[41,47–51] is carried out to first order. The small parameter of expansion is the inverse of the effective number of atoms interacting with one fixed atom.[37] In the framework of the ring approximation,

$$\alpha_{\mathbf{k}}=1-N^{-1}\sum_{\mathbf{q}}\beta_{\mathbf{q}}+\beta_{\mathbf{k}}, \tag{5}$$

where

$$\beta_{\mathbf{k}}=[A_{\mathbf{k}}+R_{\mathbf{k}}+X_{\mathbf{k}}]^{-1}, \tag{6}$$

$$A_{\mathbf{k}}=1+\frac{c(1-c)}{k_{\mathrm{B}}T}(\Phi_{\mathbf{k}}^{(2)}+\mu), \tag{7}$$

$$R_{\mathbf{k}}=\frac{(1-2c)^2}{2c(1-c)}\left(\frac{1}{I_{\mathbf{k}}}-1\right), \tag{8}$$

$$I_{\mathbf{k}}=N^{-1}\sum_{\mathbf{q}}\,[A_{\mathbf{k}-\mathbf{q}}A_{\mathbf{q}}]^{-1}, \tag{9}$$

$\Phi_{\mathbf{k}}^{(2)}$ is the Fourier transform of $\Phi_{\mathbf{R}_1,\mathbf{R}_2}^{(2)}=\Phi_{\mathbf{R}_1-\mathbf{R}_2}^{(2)}$,

$$\Phi_{\mathbf{k}}^{(2)}=\sum_{\mathbf{R}}\,\Phi_{\mathbf{R}}^{(2)}\exp(-i\mathbf{kR}), \tag{10}$$

μ is the quantity to be found from the equation

$$N^{-1}\sum_{\mathbf{q}}\,[A_{\mathbf{q}}]^{-1}=1, \tag{11}$$

T is the absolute temperature, and k_{B} is the Boltzmann constant.

Equations (5)–(11) are the generalization of Eqs. (7.6)–(7.10) in Ref. 27 by taking into account the chemical potential fluctuations and using the correct equation for determination of the chemical potential.[28] The expression for $X_{\mathbf{k}}$ is presented in Ref. 29. It consists of the sum of the terms proportional to the Fourier transforms of $\Phi_{\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3}^{(3)}$ and $\Phi_{\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3,\mathbf{R}_4}^{(4)}$. In the present paper, we assume that $X_{\mathbf{k}}$ is negligible, i.e., $X_{\mathbf{k}}\approx 0$, so that the contribution from this high-order term is comparatively small. It should be emphasized that neglect of the contribution from $X_{\mathbf{k}}$ does not mean the total neglect of the nonpair atomic interactions because the quantity $\Phi_{\mathbf{R}_1,\mathbf{R}_2}^{(2)}$ (and correspondingly $\Phi_{\mathbf{k}}^{(2)}$) already contains the contribution from such interactions [see Eqs. (B.5) and (B.6) in Ref. 23]. Below we will call the function $\Phi_{\mathbf{R}}^{(2)}$ the effective atomic interactions.

III. KKR-CPA-BASED EFFECTIVE ATOMIC INTERACTIONS

Elsewhere,[21,22] we have described in detail how the effective atomic interactions $\Phi_{\mathbf{k}}^{(2)}$ in reciprocal wave-vector space can be obtained from electronic-structure calculations. We start with the KKR-CPA description of the electronic structure of the high-T, compositionally disordered state. $\Phi_{\mathbf{k}}^{(2)}$ is determined from the response of the electronic structure of the alloy to small-amplitude concentration waves. (We note that the previous KKR-CPA-based thermodynamics results use $S_{\mathbf{R}}^{(2)}=-\Phi_{\mathbf{R}}^{(2)}$, because $S_{\mathbf{R}}^{(2)}$ is analogous to the Ornstein-Zernike direct correlation function used in the theory of nonuniform classical fluids.[18]) All electronic effects are included. In particular the alteration of charge that occurs as the atoms are rearranged is fully accounted for. The nuclei are constrained to occupy ideal fcc crystal lattice positions, so we have neglected the effect of inhomogeneous static atomic displacements. These are expected to be small for $\mathrm{Cu}_{1-c}\mathrm{Pd}_c$ alloys. Nevertheless, we took into account the *homogeneous* static atomic displacements by minimizing the alloy's total energy with respect to the lattice parameter of the underlying lattice.[52]

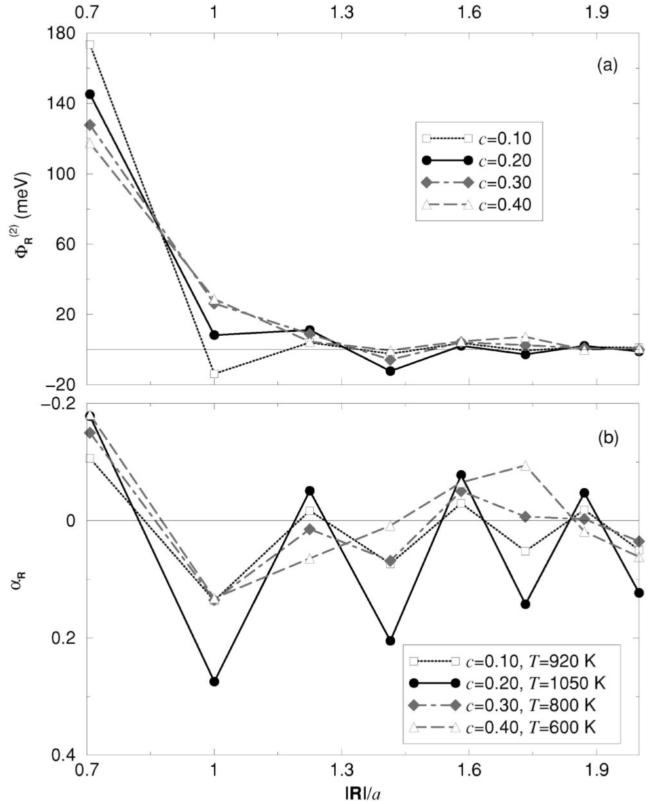

FIG. 2. The values (a) of the effective atomic interaction $\Phi_{\mathbf{R}}^{(2)}$ (at $T=1000$ K) and (b) of the SRO parameters $\alpha_{\mathbf{R}}$ calculated for a number of fcc coordination shells in a disordered fcc $\mathrm{Cu}_{1-c}\mathrm{Pd}_c$ alloy at four concentrations. Note that in part (b), the vertical axis is inverted for comparison with (a).

IV. RESULTS AND DISCUSSION

We calculated the function $\Phi_{\mathbf{k}}^{(2)}$ for disordered face-centred-cubic $\mathrm{Cu}_{1-c}\mathrm{Pd}_c$ alloys for a number of values of concentration c at $T=1000$ K. Then we used these values of $\Phi_{\mathbf{k}}^{(2)}$ to fit to a real-space expansion and give the real-space coefficients $\Phi_{\mathbf{R}}^{(2)}$ in Fig. 2 and in Table I. The SRO parameters $\alpha_{\mathbf{R}}$ obtained by integration of $\alpha_{\mathbf{k}}$ using Eqs. (4) are also presented in Fig. 2. For both $\Phi_{\mathbf{R}}^{(2)}$ and $\alpha_{\mathbf{R}}$, we see the same tendency for the period of oscillations to increase with concentration. This fact is in accordance with the experimental data that show the short-period α' ($L1_2$) and long-period α'' structures to appear below and above $c\simeq 0.285$, respectively.[53]

In Fig. 3, the dependence of $\Phi_{\mathbf{k}}^{(2)}$ calculated for a number of different values of concentration c for wave vectors along the high-symmetry lines[54] in the first Brillouin zone is shown. One can see that the position of the absolute minimum of $\Phi_{\mathbf{k}}^{(2)}$ depends on the concentration. At $c=0.10$ this

TABLE I. The values of the effective atomic interaction $\Phi_{\mathbf{R}}^{(2)}$ (in meV) calculated for disordered fcc $\mathrm{Cu}_{1-c}\mathrm{Pd}_c$ alloy at four concentrations. The Cartesian coordinates of the vector **R** are given in $a/2$ units, where a is the fcc lattice parameter.

Shell	**R**	$\lvert\mathbf{R}\rvert/a$	$c=0.10$	$c=0.20$	$c=0.30$	$c=0.40$
1	110	0.707	173.338	145.038	127.650	117.404
2	200	1.000	−13.919	8.123	26.164	28.613
3	211	1.225	3.840	11.030	8.904	4.470
4	220	1.414	−2.525	−12.347	−5.833	−0.408
5	310	1.581	3.585	2.050	4.004	4.607
6	222	1.732	−0.620	−2.925	2.448	7.215
7	321	1.871	1.293	2.065	0.757	−0.128
8	400	2.000	0.969	−1.219	−0.069	0.725
9	411	2.121	1.381	0.072	0.114	0.714
	330		−4.189	2.099	4.320	2.833
10	420	2.236	−1.819	1.089	2.090	1.213
11	332	2.345	1.292	−0.713	0.665	1.312
12	422	2.449	−3.427	4.633	3.929	0.513
13	431	2.550	1.727	−1.469	−2.718	−1.668
	510		−0.680	1.439	0.729	−0.553
14	521	2.739	1.425	−1.725	−1.075	0.419
15	440	2.828	−1.301	−1.132	0.904	2.234
16	433	2.915	−1.430	0.152	−0.158	−0.074
	530		−2.543	2.229	1.769	−0.374
17	442	3.000	1.001	−0.737	0.320	0.668

position lies on the point $X(0,1,0)$, whereas for the other concentrations, it is on the high-symmetry line $Z[0,1,\zeta]$. There is a tendency for the absolute minimum of $\Phi_{\mathbf{k}}^{(2)}$ to shift along the line $Z[0,1,\zeta]$ monotonously from point $X(0,1,0)$ to point $W(0,1,\frac{1}{2})$ with increasing concentration. Note that our results in Fig. 3 are in qualitative agreement with those presented in Fig. 3 in Ref. 55. The quantitative difference is caused by the more complete account of the electronic effects in the present study.[21,22]

We have investigated the Fermi surfaces of the corresponding disordered alloys and find that the positions of these minima correlate perfectly with the spanning vector between parallel sheets. Full details of these studies of the Fermi surfaces can be found in Ref. 52 and a comparison with experiment in Ref. 20.

In Fig. 4, we present the dependence of the peak position ζ_0 of $\alpha_{\mathbf{k}}$ (see Fig. 1) on temperature for a number of concentrations. The available experimental data[10] are also shown in Fig. 4. In each case, the lowest temperature for which the calculations were performed corresponds approximately to the critical temperature of the order-disorder phase transformation obtained within the ring approximation.[56] At $c=0.10$, there is no splitting at any temperature that was considered. The strongest temperature dependence of the peak position is observed for $c=0.20$, when the splitting of the peak at the $X(0,1,0)$ point disappears at $T\simeq 1100$ K. For concentrations $c=0.20$ upwards, there is a tendency for the temperature dependence of the peak position to diminish. As shown in Fig. 4, this is in good agreement with experiment.[10] Both our calculations and the experimental data[10] correspond to thermal equilibrium and are qualitatively different from those data which correspond to a nonequilibrium irradiated disordered state.[5] Concerning the experimental data, it should be noted that they are quite scattered (for a review see Fig. 3 in Ref. 12) and only available for a small temperature interval [see (h) and (i) curves in Fig. 4]. It is important that the experimental data[10] presented in Fig. 4 correspond to the diffuse scattering intensity rather than to the function $\alpha_{\mathbf{k}}$. Extraction of the contribution caused by static atomic displacements can change the data.[35]

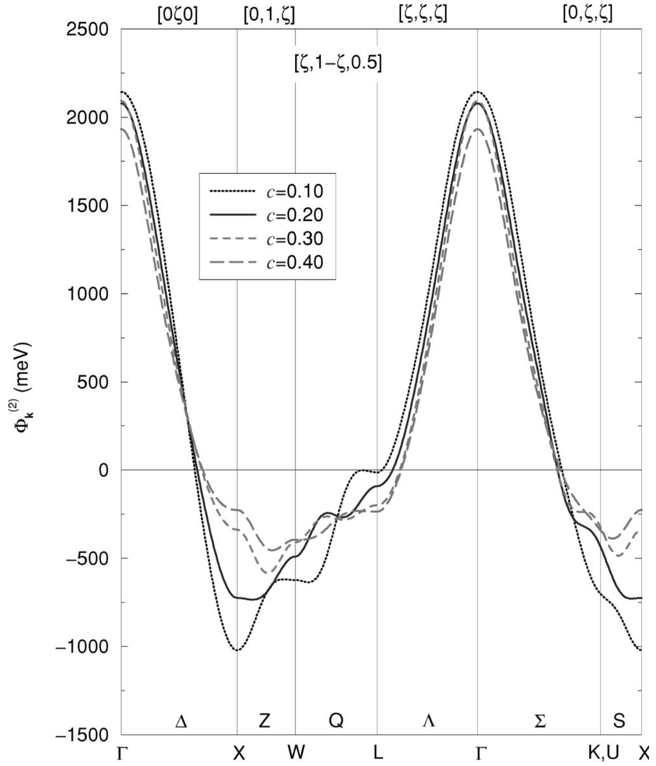

FIG. 3. The wave-vector dependence of the effective atomic interaction $\Phi_{\mathbf{k}}^{(2)}$ along the high-symmetry lines (Ref. 54) in the first Brillouin zone for disordered fcc $\mathrm{Cu}_{1-c}\mathrm{Pd}_c$ alloy at four concentrations.

In Fig. 5, the calculated SRO Fourier transform $\alpha_{\mathbf{k}}$ along the line $Z[0,1,\zeta]$ in the appropriate first Brillouin zone in the case of disordered fcc $\mathrm{Cu}_{0.79}\mathrm{Pd}_{0.21}$ alloy is shown at some temperatures. (This concentration is the same as that quoted in the experimental work.[10]) In Fig. 6, we present both the theoretical and experimental[7] dependences of the peak position ζ_0 of $\alpha_{\mathbf{k}}$ on the concentration c of disordered fcc $\mathrm{Cu}_{1-c}\mathrm{Pd}_c$ alloy at $T\approx 1000$ K. The theoretical result for $T=10\,000$ K is also shown in Fig. 6, because at such a high temperature the peak position of $\alpha_{\mathbf{k}}$ corresponds to the position of the minimum of $\Phi_{\mathbf{k}}^{(2)}$. This is easy to see from the following high-temperature approximation obtained from Eqs. (5)–(9):

$$\alpha_{\mathbf{k}}\approx 1-\frac{c(1-c)}{k_{\mathrm{B}}T}\Phi_{\mathbf{k}}^{(2)}. \tag{12}$$

As our calculations show, the temperature dependence of $\Phi_{\mathbf{k}}^{(2)}$ is weak and we can use the same function over a wide

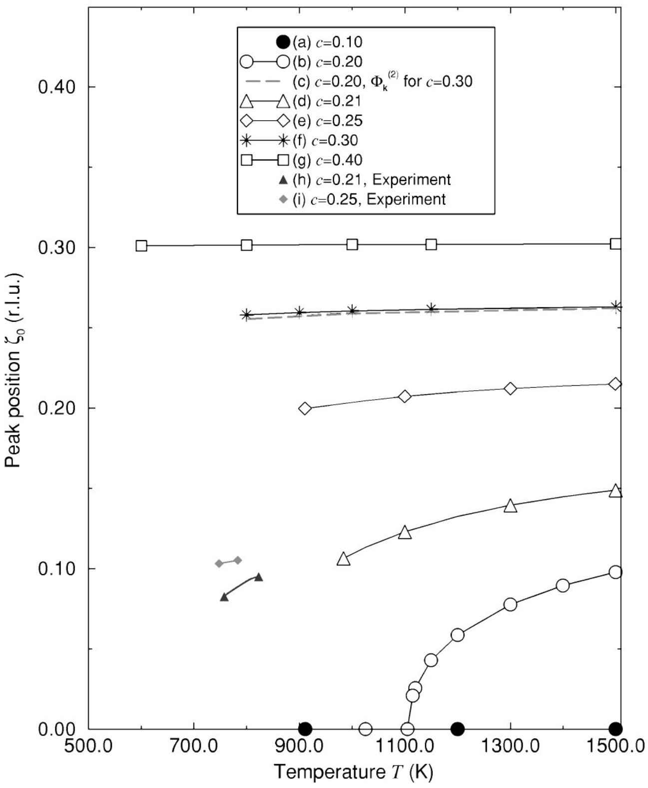

FIG. 4. The dependence of the peak position ζ_0 of $\alpha_{\mathbf{k}}$ and of the diffuse scattering intensity (in the case of experimental data) with respect to the temperature for a number of different concentrations c of the disordered fcc $Cu_{1-c}Pd_c$ alloy. (c) The data calculated at $c=0.20$ but with $\Phi^{(2)}_{\mathbf{k}}$ corresponding to $c=0.30$. (h) and (i) the experimental data (Ref. 10).

temperature range.[57] Thus, the temperature dependence of the peak position ζ_0 of $\alpha_{\mathbf{k}}$ is primarily an "entropy" effect. One can see from Eqs. (5)–(9) that the shift of the $\alpha_{\mathbf{k}}$ peak position from the position of minimum of $\Phi^{(2)}_{\mathbf{k}}$ is possible within the ring approximation due to the presence of the function $R_{\mathbf{k}}$ (and $X_{\mathbf{k}}$). Therefore, it is the function $R_{\mathbf{k}}$ which is responsible for the denoted "entropy" effect. Note that $R_{\mathbf{k}}$ is the difference between the ring and spherical model[13,21,24,25,36–40] approximations. From Fig. 6, it follows that the "entropy" effect on the peak position is strong at low concentrations and brings the theoretical results into closer agreement with experiment.

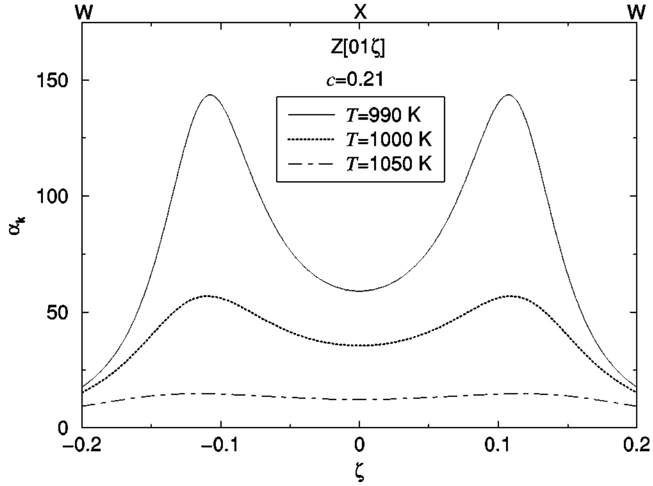

FIG. 5. The SRO Fourier transform $\alpha_{\mathbf{k}}$ along the line $Z[0,1,\zeta]$ in the case of disordered fcc $Cu_{1-c}Pd_c$ alloy calculated for a number of temperatures at $c=0.21$. For comparison with experimental data, see Fig. 2 in Ref. 10.

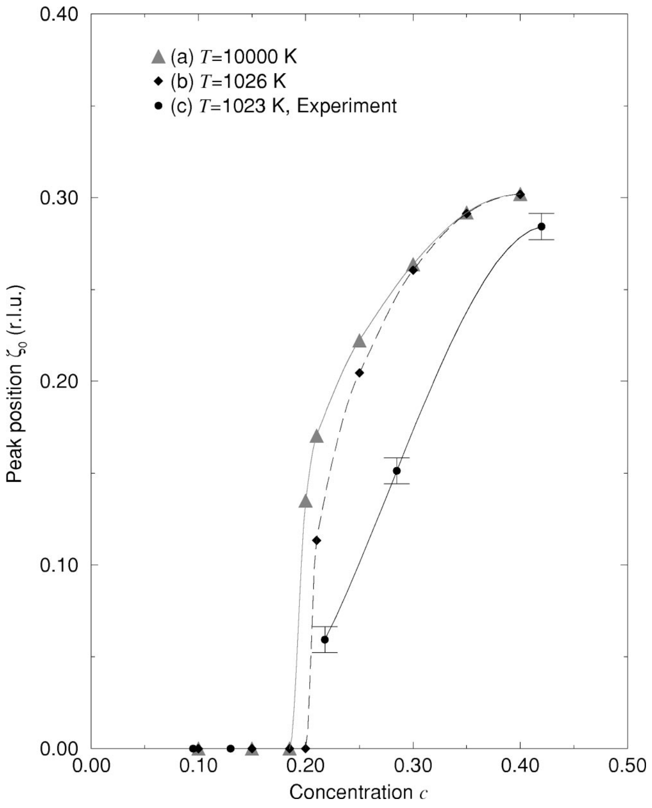

FIG. 6. The dependence of the peak position ζ_0 of $\alpha_{\mathbf{k}}$ with respect to the concentration c calculated for disordered fcc $Cu_{1-c}Pd_c$ alloy at (a) $T=10\,000$ K and (b) $T=1026$ K. (c) Experimental data (Ref. 7).

As shown in Fig. 4, the temperature dependence of the peak position of $\alpha_{\mathbf{k}}$ is remarkably different at different concentrations. The origin of this [see Eqs. (5)–(9)] can be traced to the dependence of both $\Phi^{(2)}_{\mathbf{k}}$ ("energy" effect) and $R_{\mathbf{k}}$ (entropy effect) on concentration. From Eq. (8), it follows that the entropy effect decreases when the concentration approaches 0.5. To estimate such an entropy effect, we calculated the dependence of the peak position ζ_0 of $\alpha_{\mathbf{k}}$ with respect to the temperature at $c=0.20$ but with $\Phi^{(2)}_{\mathbf{k}}$ corresponding to $c=0.30$. The result is presented in Fig. 4 [curve (c)]. One can see that the difference between two curves corresponding to the same $\Phi^{(2)}_{\mathbf{k}}$ but to the different concentrations $c=0.20$ and $c=0.30$ [curves (c) and (f) in Fig. 4, respectively] is quite small. Therefore, the entropy effect on the difference between the temperature dependence of the $\alpha_{\mathbf{k}}$ peak positions for different concentrations is not dominant.

It is a feature of the effective atomic interaction $\Phi^{(2)}_{\mathbf{k}}$ which causes the effect. We studied the behavior of the functions $\beta^{-1}_{\mathbf{k}}$, $A_{\mathbf{k}}\,R_{\mathbf{k}}$, and $I_{\mathbf{k}}$ at $c=0.20$ but with $\Phi^{(2)}_{\mathbf{k}}$ corre-

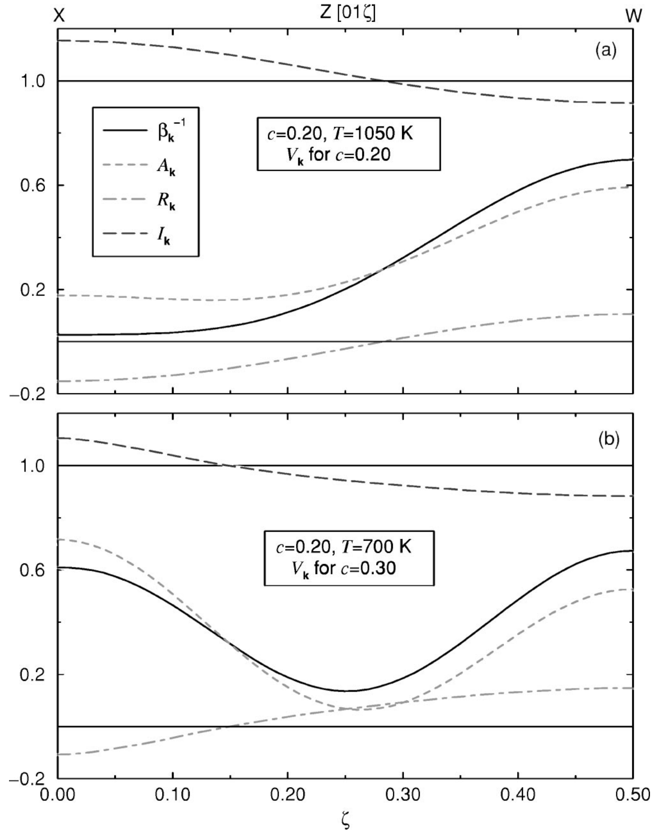

FIG. 7. Some characteristic functions corresponding to the ring approximation (see Sec. II) presented along the line $Z[0,1,\zeta]$ in the case of disordered fcc $\mathrm{Cu}_{1-c}\mathrm{Pd}_c$ alloy at (a) $c=0.20$, $T=1050$ K, and $\Phi_{\mathbf{k}}^{(2)}$ for $c=0.20$ and (b) $c=0.20$, $T=700$ K, and $\Phi_{\mathbf{k}}^{(2)}$ for $c=0.30$. The designations of the curves are the same for both parts of the figure.

sponding to both $c=0.20$ and $c=0.30$. The results are presented in Fig. 7. From this figure, one can see that, in both cases, the function $R_{\mathbf{k}}$ is of the same magnitude.[58] But the minimum of $\Phi_{\mathbf{k}}^{(2)}$ [and appropriately of $A_{\mathbf{k}}$—see Eq. (7)] corresponding to $c=0.30$ is much deeper than that at $c=0.20$. Thus, a similar contribution from the function $R_{\mathbf{k}}$ can shift the position of the minimum of $\beta_{\mathbf{k}}^{-1}$ [and correspondingly of the peak of $\alpha_{\mathbf{k}}$—see Eq. (5)] much more at $c=0.20$ than at $c=0.30$. Therefore, it is the depth of the minimum of $\Phi_{\mathbf{k}}^{(2)}$ that determines to which extent the peak position of $\alpha_{\mathbf{k}}$ depends on the temperature: the shallower the minimum, the stronger such temperature dependence.

V. CONCLUSIONS

In this paper, an approach was implemented to study the temperature and concentration dependences for atomic short-range order in disordered fcc Cu-Pd alloys. The method combines the KKR-CPA-based linear-response theory of concentration fluctuations with the ring approximation to improve the statistical mechanics descriptions. In accordance with experimental data, the fourfold splitting of the SRO Fourier transform was found to peak at about $X(0,1,0)$ and equivalent positions in reciprocal space. It was shown that such a splitting is an ‘‘energy’’ effect arising from the absolute minimum of the Fourier transform of the effective atomic interaction $\Phi_{\mathbf{k}}^{(2)}$ and, within the KKR-CPA calculations, is linked directly to nested sheets of Fermi surface.

It was found that the temperature dependence of $\Phi_{\mathbf{k}}^{(2)}$ in disordered fcc Cu-Pd alloys is weak and that the temperature dependence of the SRO peak position is an ‘‘entropy’’ effect. Nevertheless, the diminution of the temperature dependence of the SRO peak position with composition is caused by the deepening of the absolute minimum of the Fourier transform of the effective atomic interaction $\Phi_{\mathbf{k}}^{(2)}$, i.e., by an energy effect. The increase of the SRO peak splitting with composition is caused by the corresponding increase of the splitting of the absolute minimum of $\Phi_{\mathbf{k}}^{(2)}$; i.e., it is also an energy effect.

Both the calculated temperature and concentrational dependences of the SRO peak position are in good correspondence with the experimental data. Further quantitative improvement may be expected by taking into account the elastic contribution upon $\Phi_{\mathbf{k}}^{(2)}$ caused by the inhomogeneus static atomic displacements.

In real space, for both the effective atomic interaction and SRO parameters we obtained the same tendency of the increase of the period of oscillations with concentration. This feature is in accordance with the experimental data that the short- and long-period structures appear at low and high compositions of the alloy, respectively.

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*Electronic address: r_chepulskii@yahoo.com

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[56] Within the ring approximation, the critical temperature of the order-disorder phase transformation is determined by the zero value of the function $\beta_{\mathbf{k}}^{-1}$ defined in Eq. (6). Note that the study of the phase diagram of Cu-Pd alloy is not the aim of this paper and will be published elsewhere (including a detailed calculation of order-disorder phase transformation temperatures).

[57] $\Phi_{\mathbf{k}}^{(2)}$ is calculated from an integral of the product of a Fermi-Dirac function and electronic structure quantities. The temperature dependence that is included is therefore weak for temperatures less than 2000 K (Ref. 21).

[58] Following the same line of reasoning as in Ref. 12, from Eqs. (5)–(7) it is easy to conclude that the monotonous increase of $R_{\mathbf{k}}$ with ζ along the line $Z[0,1,\zeta]$ results in a shift of the minimum of $\beta_{\mathbf{k}}^{-1}$ (and thus of the maximum of $\alpha_{\mathbf{k}}$) towards the X point with respect to the minimum of $A_{\mathbf{k}}$ (and of $\Phi_{\mathbf{k}}^{(2)}$).