Nonuniform displacements of copper atoms in interstitial copper-carbon solid solutions

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Study of the nonuniform displacements of copper atoms in dilute interstitial Cu-C solid solutions is provided in the framework of the microscopic phenomenological theory of interstitial solid solutions. For the interstitial dilute copper-carbon solid solution in the copper-rich region we calculate quasielastic Kanzaki forces and nonuniform static displacements of copper atoms. Our calculations show the long-range character of the deformational interaction in dilute Cu-C alloys [S0163-1829(97)10505-7]

The problem of stability of copper-carbon solid solutions is significant for the developement of modern metal matrix composites with the aim of adding improved mechanical properties to the excellent electrical and thermal conductivity properties of copper (see, e.g., Refs. 1 and 2). Of particular interest is the possibility of developing improved high-temperature strength. Addition of particulate graphite to copper matrices permits considerable improvements in tribological properties. Thus Cu-carbon composites see regular application in sliding electrical contacts applications.

A strong deformational interaction in interstitial copper-carbon solid solutions leads to considerable nonuniform static displacements of the solvent atoms. Knowledge of values of these displacements allows us to predict the tendencies to the concentrational polymorphic transformation in the alloys with interstices. Displacements show how the lattice ''prepares'' itself for the phase transition when the concentration of alloying atoms is changed.[3] Fourier transformations of the nonuniform static displacements define also diffraction effects in ordered interstitial phases. Effects of an atomic relaxation appear to be important in a study of a phase equilibrium even in substitutional alloys (see, e.g., Ref. 4). For example, the relaxation influences on the relative stability of different ordered metal compounds (see, for example, Ref. 5), changes the phase transition temperature in alloys (see e.g., Refs. 3 and 6), etc. At the same time it is difficult to predict the influence of the type of the interstitial impurity on the values of displacements of atoms in different matrices. Displacements depend not only on relative ''geometric'' sizes of the atoms of the impurity and those of the host matrix, but also on the electron charge redistribution in the vicinity of the impurity. Thus, both a geometrical factor and a charge transfer have to be accounted for in the framework of the same formalism.

For the interstitial dilute copper-carbon solid solution in the copper-rich region we calculate quasielastic Kanzaki forces and nonuniform static displacements of copper atoms. These displacements are considered for the first and second coordination shells of the intersite carbon atom.

In our study we used the microscopic phenomenological theory of the interstitial solid solutions, which was developed by Khachaturyan.[7] It is based on the calculations of the energy caused by the elastic distortions of the lattice with interstitial atoms. This energy, $\Delta\Phi$, is given in the form

$$\Delta\Phi=\frac{1}{2}\sum_{\vec{R},\vec{R}'} A^{ij}(\vec{R}-\vec{R}')u_i(\vec{R})u_j(\vec{R}') - \sum_{\vec{R},\vec{R}',\,p=1}^{p=\nu} \vec{\bar{F}}_p(\vec{R}-\vec{R}')\vec{u}(\vec{R})C_p(\vec{R}'). \qquad (1)$$

$\Delta\Phi$ is the change of the energy, referenced to the state, when all displacements $\vec{u}(\vec{R})$ of the solvent atoms are equal to zero. $\vec{u}(\vec{R})$ is referenced to the positions of the lattice sites of pure solvent, that is, the Bravais lattice. Number p numerates ν interstice positions in the unit cell of the solvent. The position of each interstitial site may be given by the set $\{\vec{R},p\}$, where $\vec{R}$ is the radius vector of the solvent atom, determining the primitive cell. $A^{ij}(\vec{R}-\vec{R}')$ are the force constants, and $C_p(\vec{R})$ is the spinlike variable:

$$C_p(\vec{R})=\begin{cases}1 & \text{if an atom is in the interstitial position } p \text{ of the primitive cell } \vec{R},\\ 0 & \text{otherwise.}\end{cases}$$

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TABLE I. Components of the dynamic matrix A_{ij}.

A_{xx}	$4(2\beta+\alpha)-4\beta\cos\left(k_x\frac{a}{2}\right)\left[\cos\left(k_y\frac{a}{2}\right)+\cos\left(k_z\frac{a}{2}\right)\right]-4\alpha\cos\left(k_y\frac{a}{2}\right)\cos\left(k_z\frac{a}{2}\right)$
A_{yy}	$4(2\beta+\alpha)-4\beta\cos\left(k_y\frac{a}{2}\right)\left[\cos\left(k_x\frac{a}{2}\right)+\cos\left(k_z\frac{a}{2}\right)\right]-4\alpha\cos\left(k_x\frac{a}{2}\right)\cos\left(k_z\frac{a}{2}\right)$
A_{zz}	$4(2\beta+\alpha)-4\beta\cos\left(k_z\frac{a}{2}\right)\left[\cos\left(k_x\frac{a}{2}\right)+\cos\left(k_y\frac{a}{2}\right)\right]-4\alpha\cos\left(k_x\frac{a}{2}\right)\cos\left(k_y\frac{a}{2}\right)$
A_{xy}	$2\gamma\sin\left(k_x\frac{a}{2}\right)\sin\left(k_y\frac{a}{2}\right)$
A_{xz}	$2\gamma\sin\left(k_x\frac{a}{2}\right)\sin\left(k_z\frac{a}{2}\right)$
A_{yz}	$2\gamma\sin\left(k_y\frac{a}{2}\right)\sin\left(k_z\frac{a}{2}\right)$

$\overline{\vec{F}_p}(\vec{R}-\vec{R}')$ are the constants characterizing the interaction force between the solvent atom in the position $\vec{R}$ and the interstitial solute atom in the position $(p,\vec{R}')$. The sum in Eq. (1) is performed over all the lattice sites of the solvent lattice. The insertion of the interstitial atom into the solvent lattice is accompanied by two effects: (a) uniform lattice dilatation, and (b) nonuniform deformation of the lattice, that is, localized in the vicinity of interstitial atoms. Thus, the total displacement is represented in the form

$$u_i(\vec{R})=\mathcal{E}_{ij}R_j+\epsilon_i(\vec{R}) \tag{2}$$

and

$$C_p(\vec{R})=\langle c_p\rangle+\Delta c_p(\vec{R}), \tag{3}$$

$\mathcal{E}_{ij}$ is the uniform macroscopic strain, and $\epsilon_i(\vec{R})$ is the displacement referenced to the ''averaged'' lattice. $\langle c_p\rangle$ is the atomic fraction of interstitial atoms in the positions p. Making use of the Fourier transformations

$$\begin{aligned} A^{ij}(\vec{k})&=\sum_{\vec{R}} A^{ij}(\vec{R})e^{-i\vec{k}\cdot\vec{R}},\\ \vec{\epsilon}(\vec{k})&=\sum_{\vec{R}} \vec{\epsilon}(\vec{R})e^{-i\vec{k}\cdot\vec{R}}, \qquad (4)\\ \overline{\vec{F}_p}(\vec{k})&=\sum_{\vec{R}} \overline{\vec{F}_p}(\vec{R})e^{-i\vec{k}\cdot\vec{R}},\\ c_p(\vec{k})&=\sum_{\vec{R}} \Delta c_p(\vec{R})e^{-i\vec{k}\cdot\vec{R}}, \qquad (5) \end{aligned}$$

and the equilibrium condition with respect to displacements one obtains

$$\epsilon_i(\vec{k})=G^{ij}(\vec{k})\sum_{p=1}^{\nu}\overline{F_p^j}(\vec{k})c_p(\vec{k}), \tag{6}$$

where $G^{ij}(\vec{k})$ is defined by

$$G^{ij}(\vec{k})A^{jl}(\vec{k})=\delta_{il}.$$

If $u_{ij}^0(p)$ is the tensor of the coefficients of the concentrational distortion of the lattice when interstitial atoms are occupying the sublattice p, then

$$\mathcal{E}_{ij}=u_{ij}^0(p)\langle c_p\rangle,$$

and Eq. (1) may be represented in the form

$$\begin{aligned} \Delta\Phi=&-\frac{Nv}{2}\lambda_{ijlm}\sum_{p,q} u_{ij}^0(p)\langle c_p\rangle u_{lm}^0(q)\langle c_q\rangle\\ &+\frac{1}{2N}\sum_{\vec{k}} A^{ij}(\vec{k})\epsilon_i^*(\vec{k})\epsilon_j(\vec{k})\\ &-\frac{1}{N}\sum_{\vec{k}} \overline{F_p^i}(\vec{k})\epsilon_i^*(\vec{k})c_p(\vec{k}), \end{aligned} \tag{7}$$

where v is the volume of the primitive cell, N is the number of cells, and λ_{ijlm} is the Voigt shear modulus tensor.

TABLE II. Values of dynamic matrix components for the copper host matrix in the special points in the Brillouin zone. $\vec{k}$ are given in $2\pi/a$ units, and the components of the dynamic matrix A_{ij} in N/m^2.

$\vec{k}$	A_{xx}	A_{xy}	A_{xz}	A_{yz}	A_{yy}	A_{zz}
$(\frac{7}{8},\frac{3}{8},\frac{1}{8})$	37.3284	2.48883	1.03091	2.48883	23.8773	29.4489
$(\frac{7}{8},\frac{1}{8},\frac{1}{8})$	42.9	1.03091	1.03091	1.03091	23.8773	23.8773
$(\frac{5}{8},\frac{5}{8},\frac{1}{8})$	25.9338	6.00856	2.48883	2.48883	25.9338	31.5054
$(\frac{5}{8},\frac{3}{8},\frac{3}{8})$	26.5342	6.00856	6.00856	6.00856	23.2704	23.2704
$(\frac{5}{8},\frac{3}{8},\frac{1}{8})$	28.8421	6.00856	2.48883	2.48883	20.9626	23.2704
$(\frac{5}{8},\frac{1}{8},\frac{1}{8})$	30.8985	2.48883	2.48883	1.03091	17.4474	17.4474
$(\frac{3}{8},\frac{3}{8},\frac{3}{8})$	19.5039	6.00856	6.00856	6.00856	19.5039	19.5039
$(\frac{3}{8},\frac{3}{8},\frac{1}{8})$	16.8406	6.00856	2.48883	2.48883	16.8406	14.5327
$(\frac{3}{8},\frac{1}{8},\frac{1}{8})$	13.9259	2.48883	2.48883	1.03091	8.35425	8.35425
$(\frac{1}{8},\frac{1}{8},\frac{1}{8})$	1.92439	1.03091	1.03091	1.03091	1.92439	1.92439

TABLE III. Values of Fourier transform components of Kanzaki forces in the special points of the Brillouin zone. $\vec{k}$ are given in $2\pi/a$ units.

$\vec{k}$	F_x	F_y	F_z
$(\frac{7}{8},\frac{3}{8},\frac{1}{8})$	12.862	31.0516	12.862
$(\frac{7}{8},\frac{1}{8},\frac{1}{8})$	12.862	12.862	12.862
$(\frac{5}{8},\frac{5}{8},\frac{1}{8})$	31.0516	31.0516	12.862
$(\frac{5}{8},\frac{3}{8},\frac{3}{8})$	31.0516	31.0516	31.0516
$(\frac{5}{8},\frac{3}{8},\frac{1}{8})$	31.0516	31.0516	12.862
$(\frac{5}{8},\frac{1}{8},\frac{1}{8})$	31.0516	12.862	12.862
$(\frac{3}{8},\frac{3}{8},\frac{3}{8})$	31.0516	31.0516	31.0516
$(\frac{3}{8},\frac{3}{8},\frac{1}{8})$	31.0516	31.0516	12.862
$(\frac{3}{8},\frac{1}{8},\frac{1}{8})$	31.0516	12.862	12.862
$(\frac{1}{8},\frac{1}{8},\frac{1}{8})$	12.862	12.862	12.862

The matrix of the force constants on the first coordination shell has the following symmetry (see, for example, Ref. 8):

$$\begin{Bmatrix} \beta & \gamma & 0 \\ \gamma & \beta & 0 \\ 0 & 0 & \alpha \end{Bmatrix}. \tag{8}$$

The force constants α, β, and γ may be calculated from the experimetally measured elastic constants C_{11}, C_{12}, and C_{44}, according to the following relations:[8]

$$\alpha = 1/2(C_{11}/2 - C_{44}),$$

$$\beta = -1/4C_{11},$$

$$\gamma = -1/4(C_{12}/2 - C_{44}). \tag{9}$$

All these equations (9) are written in the lattice parameter units. Using the elastic constants from Ref. 12 we obtained the matrix of the force constants (8):

$$\begin{Bmatrix} 3.0 & 3.52 & 0 \\ 3.52 & 3.0 & 0 \\ 0 & 0 & -0.215 \end{Bmatrix}. \tag{10}$$

Performing the Fourier transformation (4) for $A^{ij}(\vec{R})$ we obtain the dynamic matrix in the reciprocal space. Matrix elements A^{ij} are presented in Table I. The Fourier transform of the vector of Kanzaki forces is expressed in terms of perfect

TABLE IV. Phonon frequencies of copper in Brillouin zone points. $\vec{k}$ points are in $2\pi/a$.

$\vec{k}$ points	Frequencies (10^{12} s^{-1})	
	Theory	Experiment (taken from Ref. 9)
(001)	7.672	7.40
	5.525	4.88
$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	6.880	7.56
	4.526	3.55
$(\frac{1}{2},\frac{1}{2},0)$	6.195	6.51
	5.425	5.33
	4.526	3.40

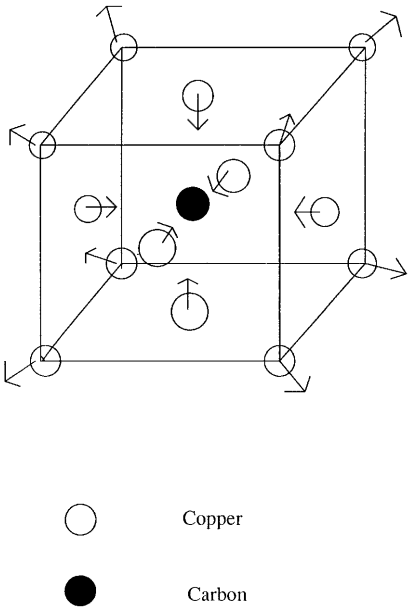

FIG. 1. Schematics of nonuniform displacements of copper atoms in interstitial copper-carbon solid solutions. Open circles are copper atoms. The solid circle is a carbon atom. Vectors show the direction of the displacements.

lattice elastic constants for a pure matrix and of the value $\hat{\mathbf{u}}$, which is the coefficient of the uniform concentrational dilatation of the lattice,[7]

$$\vec{F}(\vec{k}) = -i\frac{a^2}{2}(C_{11}+2C_{12})\hat{\mathbf{u}}\left(\sin\frac{k_x a}{2}, \sin\frac{k_y a}{2}, \sin\frac{k_z a}{2}\right), \tag{11}$$

where $\hat{\mathbf{u}} = a^{-1}(da/dc)$. a is the lattice parameter in an alloy. c is the atomic fraction of the interstitial atoms in the alloy.

In our calculations, the results of which are in Tables II, III, and IV, we use the model of the dilute Cu-C interstitial solid solution with carbon atoms which statistically occupy the octahedral interstitial positions in the fcc lattice of the host copper matrix. In this case there is only one sublattice of such positions. Thus $p=1$ and the atomic fraction c of carbon in Cu-C solid solution may be calculated from the relation

$$c = \frac{\Sigma_p c_p}{1+\Sigma_p c_p} = \frac{c_1}{1+c_1}. \tag{12}$$

The averaged value of the atomic volume may be obtained from the Zen's law. In our calculations we assumed $c_1 = 0.02$ at. % and obtained $\hat{\mathbf{u}} = 0.271$. The atomic volumes of copper and carbon were taken from Ref. 10, where these volumes were extrapolated from the experimental data to zero temperature. The elements of the dynamic matrix (Table II) and the Fourier transform of the vector of Kanzaki forces (Table III) were calculated in the special points of the Brillouin zone.[11]

The quality of the dynamical matrix calculations may be checked after carrying out diagonalization of this matrix and a comparison of the obtained phonon frequencies in some Brillouin zone points with the experimental data (see Table IV). The average error in phonon frequency calculations is

about 13.5%. This error encourages us to use the calculated values of the matrix elements A_{ij} (Table II) and the Fourier transform of the vector of Kanzaki forces (Table III) in the calculations of the nonuniform displacements of copper atoms in dilute Cu-C solid solutions.

The interstitial carbon atom was situated in the point (0,0,0), while copper atoms were located in points of types $0.5a(1,0,0)$ and $0.5a(1,1,1)$; see Fig. 1. These points correspond to the first and second nearest-neighbors (NN) atoms, respectively. The results of our calculations in accordance with Eq. (6) show that copper atoms of the first coordination shell move to the carbon atom and of the second NN move from the carbon (Fig. 1). The oscillating character of these displacements is the sequence of the oscillatory term which represents the Fourier transforms of the vector of Kanzaki forces [see Eq. (11)]. We are talking here about the motion relative to the positions in the uniformly distorted lattice. The values of the displacements on the first and second coordination shells are $\epsilon_1 = 0.98$ a.u. and $\epsilon_2 = 0.27$ a.u. The directions of this displacements are shown in Fig. 1.

It is of interest to compare this result with the values of displacements in the dilute Al-C interstitial solid solution.[13] In Al-C $\epsilon_1 = 0.29$ a.u. and $\epsilon_2 = 0.04$ a.u., while $\hat{\mathbf{u}} = 0.19$.[14] The relative displacements in the Cu-C alloy for the first and the second NN's are 14.4% and 4% from the lattice parameter. The same values for Al-C are much smaller and are equal to 3.7% and 0.55%, respectively. Such a behavior corresponds well with the balance between elastic and Coulomb forces in the compared solid solutions. The volume of the octahedral intersite in copper is much smaller than in aluminum. Thus the elastic response of the copper host on the penetration of a carbon atom is larger than the corresponding response of an aluminum matrix ($\hat{\mathbf{u}}_{\text{Cu-C}} > \hat{\mathbf{u}}_{\text{Al-C}}$). At the same time the values of the effective charge of the Al ion is larger than the Cu ion. This factor leads to the increase of the Coulomb repulsion between the carbon interstitial and the host atom in the Al-C solid solution and the modulus of the displacement vector $\boldsymbol{\epsilon}$ in the Cu-C solid solution increases. The vector of displacements of the second NN $\boldsymbol{\epsilon}_2$ in comparison with the $\boldsymbol{\epsilon}_1$ is 3 times smaller in Cu-C and 5 times smaller in Al-C. This result shows the long-range character of the deformational interaction in dilute Cu-C alloys in comparison with Al-C ones.

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