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ORDERING ENERGY OF Mo-Ni 10.7% Mo ALLOY

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This paper deals with the determination of Mo-Ni 10.7% Mo alloy ordering energy for the three first coordination shells. Calculations have been carried out on the basis of short range order parameters measured for the alloy monocrystal and cited in Spruiell's and Stansbury's paper. A pair model has been adopted in the analysis as well as the so-called linear approximation of the solution of the correlation function equations cited by Clapp and Moss in their paper.

1. *Introduction*

The purpose of this research was to find a method for determining the ordering energy in an AB type alloy for successive coordination shells on the basis of experimentally determined values of short range parameters. Mo-Ni 10.7% Mo alloy of fcc structure was used as a model. Let us consider an AB type alloy with two sublattices α, β and of atom concentration C_A and C_B respectively. The ordering energy for succesive coordination shells of r_i radius is defined as follows:

$$V(r_i) = \tfrac{1}{2}(V^{AA}+V^{BB}-2V^{AB}),$$

where V^{AA}, V^{BB}, V^{AB} are interaction energies of the atom pairs AA, BB and AB respectively. The short range order in the AB type alloy may be described by Cowley's short range order parameters

$$\alpha_{lmn} = 1-\frac{p_{AB}(r_{lmn})}{C_A C_B},$$

where $\vec{r}_{lmp} = \frac{1}{2}l\vec{a}_1+\frac{1}{2}m\vec{a}_2+\frac{1}{2}n\vec{a}_3$ is the vector linking the first atom considered with the next one at a site denoted l, m, n; $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ are cubic lattice translations. The formula is valid for a fcc structure. $p_{AB}(r_{lmn})$ denotes the probability that atoms spaced at r_{lmn}

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would take position within the α and β lattices, respectively. Fourier transforms $\alpha(k)$ and $V(k)$ for order parameters α_{lmn} and ordering energy V_{lmn} define these quantities within reciprocal space. Thus the following relationships may be written:

$$\alpha_{lmn} \equiv \alpha(r_i) = \frac{1}{v_k} \int d^3k\alpha(k) \exp(-2\pi i\vec{k}\cdot\vec{r}_j), \tag{1}$$

$$V_{lmn} \equiv V(r_i) = \frac{1}{v_k} \int d^3kV(k) \exp(-2\pi i\vec{k}\cdot\vec{r}_f), \tag{2}$$

where k — vector of the reciprocal lattice, v_k — unit cell volume within reciprocal space According to the results obtained by Clapp and Moss [2], who assumed the so-called linear approximation to the solution of correlation function equations, the following relationship exists between $\alpha(k)$ and $V(k)$ transforms:

$$\alpha(k) = \frac{C}{1+\dfrac{2C_A C_B V(k)}{k_B T}}, \tag{3}$$

where k_B — Boltzmann's constant, T — temperature, C — constant selected so that the condition

$$\alpha_{000} = \frac{1}{v_k} \int d^3k\alpha(k) = 1 \tag{4}$$

is satisfied. When using the inverse Fourier transform we obtain from equation (1) the relationship

$$\alpha(k) = \frac{1}{v_k} \int d^3r\alpha_{lmn} \exp 2\pi i\vec{k}\cdot\vec{r}_j. \tag{5}$$

Equation (3) allows one to determine $V(k)$ values on the basis of the known $\alpha(k)$ values. When adopting the inverse Fourier transform in the calculations we obtain from $V(k)$ the values of simple lattice energy $V(r_i)$.

2. *Experimental part*

In our research we have made use of the values of short range order parameters $\alpha(r_i)$ for Mo-Ni 10.7% specified in paper [1]. The measurements were carried out on a monocrystal of the alloy quenched from 1273 K in iced water. Under the measurement conditions the alloy had fcc structure. The measurement technique as well as the method adopted for parameter determination are specified in paper [1]. In Table I are listed the parameters defined in [1] and adopted in the present calculations.

TABLE I

Three dimensional short range order parameters for Mo-Ni 10.7% Mo

lmn	α_{lmn}	lmn	α_{lmn}
0 0 0	1.000	5 2 1	−0.005
1 1 0	−0.250	4 4 0	0.013
2 0 0	0.140	5 3 0	−0.010
2 1 1	0.168	4 3 3	0.000
2 2 0	−0.110	4 4 2	0.000
3 1 0	−0.061	6 0 0	−0.022
2 2 2	−0.126	6 1 1	0.012
3 2 1	0.043	5 3 2	0.000
4 0 0	0.093	6 2 0	0.002
4 1 1	−0.068	5 4 1	0.007
3 3 0	−0.035	6 2 2	0.000
4 2 0	0.033	6 3 1	0.000
3 3 2	0.016	4 4 4	0.000
4 2 2	0.003	5 5 0	0.000
5 1 0	0.023	7 1 0	0.006
4 3 1	0.000		

3. *Calculation of short range order parameters by means of Fourier transform*

Since for a fcc lattice $V = 1/a^3$ the expression for $\alpha_{lmn} = \alpha(r_i)$ has the form

$$\alpha_{lmn} = a^3 \int d^3k\alpha(k) \exp(-2\pi i\vec{k}\cdot\vec{r}), \tag{6}$$

we obtain the relationship

$$\alpha(k) = C_1 \sum_{l'm'n'} \alpha_{l'm'n'} \exp 2\pi i\vec{k}'\cdot\vec{r}'. \tag{7}$$

Since

$$\vec{k}\cdot\vec{r} = \tfrac{1}{2}(lh_1+mh_2+nh_3),$$

the form of the expressions for α_{lmn} and $\alpha(k)$ will be

$$\alpha_{lmn} = a^3 \int d^3k\alpha(k) \exp[-i\pi(lh_1+mh_2+nh_3)],$$

$$\alpha(k) = C_1 \sum_{l'm'n'} \alpha_{l'm'n'} \exp[i\pi(l'h_1+m'h_2+n'h_3)],$$

$$\alpha_{lmn} = (2\pi)^3 C_1 a^3 \sum_{l'm'n'} \alpha_{l'm'n'}\delta[\pi(l'-l)]\delta[\pi(m'-m)]\delta[\pi(n'-n)] = (2\pi)^3 C_1 \alpha_{lmn}. \tag{8}$$

Hence $C_1 = 1/(2\pi)^3$. Thus the expression for $\alpha(k)$ takes the form

$$\alpha(k) = \frac{1}{(2\pi)^3} \sum_{lmn} \alpha_{lmn} \exp[i\pi(lh_1+mh_2+nh_3)]. \tag{9}$$

Because of the crystal symmetry the imaginary part of the expression considered above may be disregarded. Finally we obtain for $\alpha(k)$ the relationship

$$\alpha(k) = \frac{1}{(2\pi)^3} \sum_{lmn} \alpha_{lmn} \cos(\pi l h_1 + \pi m h_2 + \pi n h_3). \tag{10}$$

4. Calculation of V(k) energy

The interaction energy within reciprocal space $V(k)$ is calculated in a similar way as the $\alpha(k)$ quantity. The form of the energy is as follows:

$$V(k) \equiv V(h_1, h_2, h_3) = \frac{1}{(2\pi)^3} \sum_{lmn} V_{lmn} \cos \pi(l h_1 + m h_2 + n h_3). \tag{11}$$

Now we calculate the value of the $V(k)$ energy per 1 equivalent site in the fcc lattice. For this purpose we will plot in figure 1 the simple lattice vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$ as well as the arrangement of the atoms at eight equivalent lattice sites in reference to a given atom assumed to be the centre. Since $\vec{a}_1, \vec{a}_2, \vec{a}_3$ vectors may have positive and negative senses and the lmn quantities may take on both positive and negative values, we can write for $V(k)$ energy the following relationship

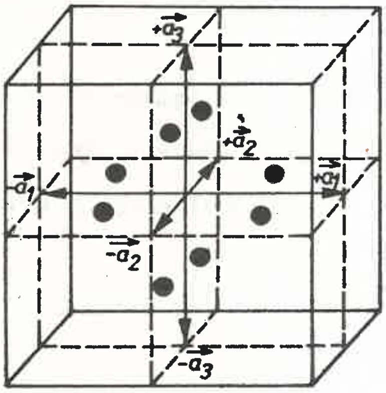

Fig. 1. Simple lattice vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$ as well as atom arrangement at eight equivalent sites

$$V(k) = \frac{1}{(2\pi)^3} \sum_{lmn} V_{lmn} \cos \pi(\pm l h_1 \pm m h_2 \pm n h_3)$$

$$= \frac{1}{(2\pi)^3} \sum_{lmn} V_{lmn}[\cos \pi(l h_1 + m h_2 + n h_3) + \cos \pi(-l h_1 - m h_2 - n h_3)$$

$$+ \cos \pi(l h_1 + m h_2 - n h_3) + \cos \pi(-l h_1 - m h_2 + n h_3)$$

$$+\cos\pi(lh_1-mh_2+nh_3)+\cos\pi(-lh_1+mh_2-nh_3)$$

$$+\cos\pi(-lh_1+mh_2+nh_3)+\cos\pi(lh_1-mh_2-nh_3)$$

$$=2[\cos\pi(lh_1+mh_2+nh_3)+\cos\pi(lh_1+mh_2-nh_3)+\cos\pi(lh_1-mh_2+nh_3)$$

$$+\cos\pi(-lh_1+mh_2+nh_3)]. \qquad (12)$$

After a trigonometrical transformation we obtain the formula below:

$$V(k)=\frac{1}{(2\pi)^3}\sum_{lmn} 8V_{lmn}\cos\pi lh_1\cos\pi mh_2\cos\pi nh_3. \qquad (13)$$

For an equivalent fcc lattice site the value of $V(k)$ energy will be

$$V(k)=\frac{1}{(2\pi)^3}\sum_{lmn} V_{lmn}\cos\pi lh_1\cos\pi mh_2\cos\pi nh_3. \qquad (14)$$

5. *Calculation of the ordering energy for the first three coordination shells*

Figures 2, 3 and 4 show the arrangement of the atoms within the first, second and third coordination shells of the fcc structure respectively. In Table II there are specified the coordinates of one of the atoms within the successive coordination shells as well as the respective coordination numbers. From equation (14) we may calculate values for each coordination shell

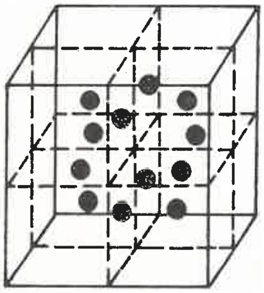
Fig. 2

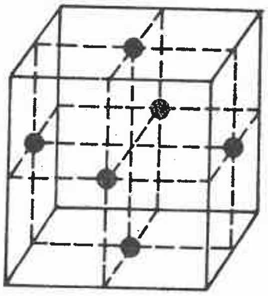
Fig. 3

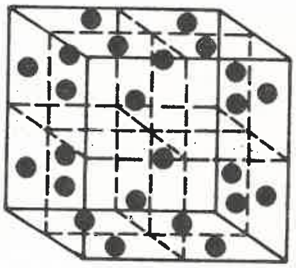
Fig. 4

Fig. 2. Atom arrangement within the first coordination shell
Fig. 3. Atom arrangement within the second coordination shell
Fig. 4. Atom arrangement within the third coordination shell

$$V_{lmn}=(2\pi)^3\int_0^2 dh_1\int_0^2 dh_2\int_0^2 dh_3 V(k)\cos\pi lh_1\cos\pi mh_2\cos\pi nh_3. \qquad (15)$$

TABLE II

Atom arrangement within individual coordination shells of an fcc lattice

Shell No	Coordination No Z_i	Atom coordinates
1	12	1/2 1/2 1/2
2	6	1 0 0
3	24	1 1/2 1/2

$V(k)$ values are obtained from formula (3)

$$V(k) = \frac{k_B T}{2C_A C_B[\alpha(k)-1]}. \tag{16}$$

Inserting this value into equation (15) we obtain the expression for V_{lmn}:

$$V_{lmn} = (2\pi)^3 \int_0^2 dh_1 \int_0^2 dh_2 \int_0^2 dh_3 \frac{k_B T}{2C_A C_B[\alpha(k)-1]}. \tag{17}$$

6. *Results*

The following parameters have been adopted in the calculation of the ordering energy for an Mo-Ni 10.7% Mo alloy: $C_A = 0.107$, $C_B = 0.893$, $T = 1273$ K. The calculations have been carried out using a program designed for a CYBER computer.

The ordering energy values obtained are listed in Table III.

TABLE III

Ordering energy values for Mo-Ni 10.7% Mo alloy

Shell No	Ordering energy [eV]
1	58.07×10^{-3}
2	-57.31×10^{-3}
3	-20.82×10^{-3}

7. *Conclusions*

The calculation method adopted in our research allowed the determination of the value of the ordering energy for three successive coordination shells. The correctness of the results obtained when using this method depends on how far the conclusions resulting from the so called linear approximation of the linear correlation function solution is valid for the alloy considered. The accuracy of the results depends largely on the accuracy of the experimental determination of the short range order parameters. The positive ordering energy for the first coordination shell shows that majority of the twelve nearest neighbours are unlike the atom at the centre. The change of the sign of the energy for the second and the third coordination shells indicates that majority from among six and twenty four atoms, respectively, are the same as the atom at the centre. The energy values obtained in our research agree as to order of magnitude with analogous results for other alloys [3].

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