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LONG-RANGE AND SHORT-RANGE ORDER IN INTERSTITIAL COMPOUNDS $M_2X$ WITH SPECIAL REFERENCE TO $V_2C$ AND Nb$_2$C

K. HIRAGA and M. HIRABAYASHI

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Résumé. — Les conditions d’existence de structure cristalline pour cinq composés de Hägg, $V_2C$, Nb$_2$C, Ta$_2$C, Co$_2$C et V$_2$N, sont déterminées dans un modèle basé sur l’interaction de paires entre des rangées atomiques interstitielles parallèles à l’axe c du réseau métallique hexagonal. Le spectre de diffusion d’un ordre à courte distance est étudié par diffraction électronique de $V_2C$ et Nb$_2$C trempés à partir de températures élevées et discuté en comparant avec les résultats des calculs basés sur ce modèle.

Abstract. — The existence conditions of the crystal structures of five Hägg compounds, $V_2C$, Nb$_2$C, Ta$_2$C, Co$_2$C and V$_2$N, are determined in the pair-wise interaction model regarding interstitial atom rows parallel to the $c$ axis of hcp metal lattice. Short-range order diffuse scattering is studied by electron diffraction on $V_2C$ and Nb$_2$C quenched from high temperatures, and discussed in comparison with calculations based on this model.

1. Introduction. — In so called Hägg compounds in which the metal structure is either fcc or hcp, there is one octahedral interstitial site per metal atom. When a substantial fraction of the octahedral sites are not occupied, the ordering of interstitial atoms occurs at low temperatures. In many transition metal carbides and nitrides with the composition $M_2X$, in which the metal lattice is hcp and half of the octahedral sites are vacant, it is known to exist varieties of the ordered octahedral occupations of interstitial atoms; e.g. CdI$_2$ antitype (or C6 type), CaCl$_2$ antitype, $\alpha$-Fe$_2$N type, $\zeta$-Fe$_2$N type and $\xi$-Nb$_2$C type (figure 1) [1, 2]. High-temperature crystal structures of $M_2X$ are tentatively assigned to the L’3 type in which the distribution of interstitial atoms is random. However, the real arrangement is not elucidated yet.

In this paper, first we analyze these five ordered structures of $M_2X$ in the pair-wise interaction model regarding pairs of interstitial atom rows, rather than individual atoms, parallel to the $c$ axis of the hcp metal lattice. On the basis of this consideration, we propose the existence conditions of these structures as functions of the ratios of interaction energies up to the third neighbor rows. Further the short-range order diffuse scattering is observed by the electron diffraction study on ($V_Nb_{1-x}$)$_2C$ quenched from high temperatures, and interpreted well by taking reasonable values of the ratios of interaction energies.

2. Pair-wise interaction model regarding interstitial atom rows. — The ordered distributions of interstitial atoms in the five $M_2X$ structures mentioned above are illustrated in figure 1. These structures are described as regular arrangements of interstitial atom rows parallel to the $c$ axis, where the interstitial atoms occupy alternately the octahedral sites with the interatomic distance $c_0$ that is the lattice constant of the hcp metal cell. As we deal mostly with the structures of carbides, the interstitial atom rows are named $C$-v rows hereafter. On the bases of this construction, the configurational energy of these structures is given as a function of the pair-wise interactions between the $C$-$v$ rows. If we designate the interactions of a like or equivalent pair and of an unlike or inequivalent pair at the $j$th neighbor as $V_j^l$ and $V_j^u$, respectively (figure 2)

$$E = \sum p_j Z_j v_j$$  \hfill (1)

$$v_j = V_j^l - V_j^u, \quad \hfill (2)$$
where $p$ is the probability of like pairs, $Z$ is the coordination number, and $v$ is the ordering energy. If $v$ is negative, like pairs are preferentially formed, and vice versa. In Table I are listed the values of $p_1$, $p_2$, and $p_3$ for the five structure types. The relative stability of these structures is readily determined by taking into account the pair interactions up to the third neighbors. The inter-row distances for the 1st, 2nd and 3rd neighbors are $a_0$, $\sqrt{3}a_0$ and $2a_0$, respectively.

**Table I**

<table>
<thead>
<tr>
<th>Structure type</th>
<th>Probability $p_1$</th>
<th>Probability $p_2$</th>
<th>Probability $p_3$</th>
<th>Designation in figures 1 and 3</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anti-CdI$_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$a$</td>
<td>Ta$_2$C, Ti$_2$O</td>
</tr>
<tr>
<td>Anti-CaCl$_1$</td>
<td>1/3</td>
<td>1/3</td>
<td>1/3</td>
<td>$b$</td>
<td>Co$_2$C, Co$_3$N</td>
</tr>
<tr>
<td>$\varepsilon$-Fe$_2$N</td>
<td>1/3</td>
<td>1/3</td>
<td>1/3</td>
<td>$c$</td>
<td>V$_2$N, Nb$_2$N</td>
</tr>
<tr>
<td>$\xi$-Fe$_2$N</td>
<td>1/3</td>
<td>2/3</td>
<td>1/3</td>
<td>$d$</td>
<td>V$_2$C, Mo$_2$C</td>
</tr>
<tr>
<td>$\xi$-Nb$_2$C</td>
<td>2/3</td>
<td>1/3</td>
<td>1/3</td>
<td>$e$</td>
<td>Nb$_2$C</td>
</tr>
</tbody>
</table>

Figure 3 shows the existence regions for the five structures as functions of the ordering energy $v_1$, $v_2$, and $v_3$. It is noted that the V$_2$C structure (d) is stable only in the limited region of $v_1/v_3 > 0$ and $v_2/v_3 < 2$, neighboring the region of Nb$_2$C (e), in the case of $v_3 > 0$. This relation is examined by diffuse scattering studies on (V$_x$Nb$_1$-x)$_2$C.

3. Diffuse scattering in electron diffraction patterns.

As shown in figures 4 and 5, diffuse scattering due to the short-range ordering of C-v rows is observed in the electron diffraction patterns of V$_2$C and Nb$_2$C quenched from 1200 and 1600°C, respectively. These temperatures are higher than the transition temperatures $T_s$ which are reported as about 800°C for V$_2$C [3] and 1230°C for Nb$_2$C [4] (1). The diffuse scattering is lying only on the reciprocal lattice planes of $l = 2n \pm 1$ normal to the $c^*$ axis. The diffuse intensity distribution of V$_2$C shows a weak maximum near $1/2,0,1$ in the $k = 0$ plane, two broad maxima near $1/3,1/3,1$ and $2/3,2/3,1$ in the $h = k$ plane, and three maxima near $1/2,1/4,1,1,1/2,1$ and $3/2,3/4,1$ in the $h = 2k$ plane. In Nb$_2$C, the diffuse scattering is observed at about the reciprocal lattice points $0,l,10,l,11,l,21,l$ et al. with $l = 2n \pm 1$. This scattering seems to have a ring shape with the radius of about 1/5 of the distance from 00.1 to 10.1, since the intensity distribution around 00.1 is similar in the three reciprocal lattice planes.

Since the diffuse scattering is concentrated only on the $l = 2n \pm 1$ planes, the interatomic distance of carbon along the $c$ axis remains to be $c_0$, as that of the C-v rows in the long-range ordered structures (figure 1).

(1) Although the higher temperature modifications of V$_2$C and Nb$_2$C with the $\varepsilon$-Fe$_2$N type have been reported in the literatures [3, 4, 5, 6], no evidence for the presence of this structure is obtained in the quenched specimens. Consequently the quenching temperatures are thought to be high enough above the disordering transition points.
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correlations of the C-v rows. The intensity distribution of diffuse scattering is given by the formula [7]

\[ I(k) = \frac{c}{1 - \frac{T_c}{T} \frac{v(k)}{v(k_m)}}, \]  

(3)

where \( c \) is a normalization constant, and \( k_m \) is the reciprocal lattice point of minimum \( v(k) \) which is the Fourier transform of the ordering energy \( v \). The observed diffuse intensity distributions are compared with the calculated curves of \( I(k) \) as functions of \( v_1 \), \( v_2 \) and \( v_3 \). As shown in figures 4 and 5, good agreement is obtained for \( V_2C \) with the ratios \( v_1/v_3 = 7 \) and \( v_2/v_3 = 1.5 \) (\( v_3 > 0 \)), and for \( Nb_2C \) with \( v_1/v_3 = -0.8 \) and \( v_2/v_3 = -0.2 \) (\( v_3 > 0 \)), assuming \( T_c/T = 0.95 \).

A series of work are done on the pseudobinary carbies \((V,Nb,Ta)_xC\). The results reveal that the evaluated values of \( v_1/v_3 \) and \( v_2/v_3 \) change continuously with composition \( x \), lying along the boundary between the regions of \( \xi \)-Fe \(_2\)N and anti-CaCl \(_2\) types in figure 2(B). Similar studies of \((Nb,Ta)_xC\) are now in progress.

4. Conclusion. — The existence conditions of the five ordered structures of hcp Hågg compounds \( M_xX \) were determined as functions of the pair-wise interactions between the interstitial atom rows up to the third neighbors. The electron diffraction study on \((V_2Nb_{1-x})C\) quenched from \( 1200-1600 \) °C revealed that the carbon atoms occupy every second octahedral sites along the \( c \) axis keeping the C-v-C sequences, and the C-v rows distribute with short-range ordered configurations. The ratios of ordering energies between the C-v rows, \( v_1/v_3 \) and \( v_2/v_3 \), are evaluated quantitatively for \( V_2C \) and \( Nb_2C \).

References