LONG-RANGE AND SHORT-RANGE ORDER IN INTERSTITIAL COMPOUNDS M2X WITH SPECIAL REFERENCE TO V2C AND Nb2C

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LONG-RANGE AND SHORT-RANGE ORDER IN INTERSTITIAL COMPOUNDS M₂X WITH SPECIAL REFERENCE TO V₂C AND Nb₂C

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Résumé. — Les conditions d'existence de structure cristalline pour cinq composés de Hägg, V_2C, Nb_2C, Ta_2C, Co_2C et V_2N, 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_2C 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_2C, Ta_2C, Co_2C and V_2N, 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_2C 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. CdI₂ antitype (or C6 type), CaCl₂ antitype, ε-Fe₂N type, ζ-Fe₂N type and ξ-Nb₂C 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 $(V_xNb_{1-x})_2C$ quenched from high temperatures, and interpreted well by taking reasonable values of the ratios if 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 jth neighbor as V_j^e and V_j^i, respectively (figure 2)
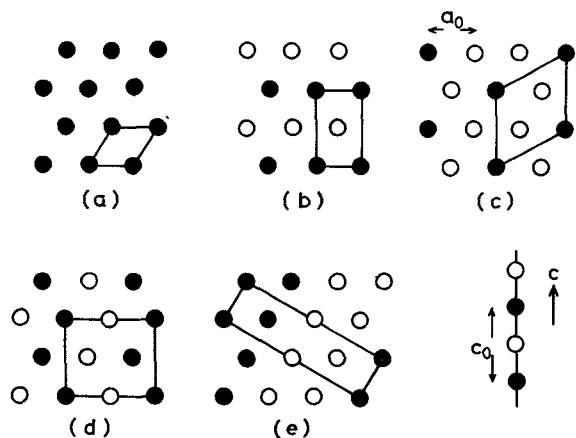

FIG. 1. — Ordered structures of interstitial atoms in the M_2X compounds. Views parallel to the c axis ; (a) CdI₂ antitype, (b) CaCl₂ antitype, (c) ε-Fe₂N type, (d) ζ-Fe₂N type, (e) ξ-Nb₂C type. Full and open circles correspond to interstitial atoms and vacant sites, respectively. The superstructure cells are indicated by full lines.
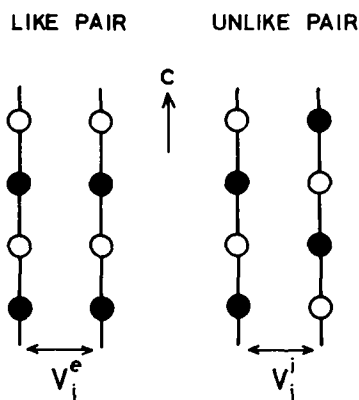
$$E = \sum_j p_j Z_j v_j \qquad (1)$$

$$v_j = V_j^e - V_j^i , \qquad (2)$$

LIKE PAIR   UNLIKE PAIR

FIG. 2. — Like and unlike pairs of the $C\text{-}v$ rows parallel to the c axis.

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 $2\, a_0$, respectively.

TABLE I

Probabilities of like-pairs of the interstitial atom rows in M₂X *structures*

Structure type	Probability			Examples	Designation in figures 1 and 3
	p_1	p_2	p_3		
Anti-CdI₂	1	1	1	Ta₂C, Ti₂O	a
Anti-CaCl₂	1/3	1/3	1	Co₂C, Co₂N	b
ε-Fe₂N	1/3	1	1/3	V₂N, Nb₂N	c
ζ-Fe₂N	1/3	2/3	1/3	V₂C, Mo₂C	d
ζ-Nb₂C	2/3	1/3	1/3	Nb₂C	e

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 V₂C 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 Nb₂C (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 V₂C and Nb₂C quenched from 1 200 and 1 600 °C, respectively. These temperatures are higher than the transition temperatures T_c which are reported as about 800 °C for V₂C [3] and 1230 °C for Nb₂C [4] ([1]). The diffuse scattering is lying only on the reciprocal lattice planes of $l = 2\, n \pm 1$ normal to the c^* axis. The diffuse intensity distribution of V₂C 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 $h = 2\, k$ plane. In Nb₂C, the diffuse scattering is observed at about the reciprocal lattice points 00.l, 10.l, 11.l, 21.l et al. with $l = 2\, n \pm 1$. 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.l is similar in the three reciprocal lattice planes.

Since the diffuse scattering is concentrated only on the $l = 2\, n \pm 1$ 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 V₂C and Nb₂C with the ε-Fe₂N 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.
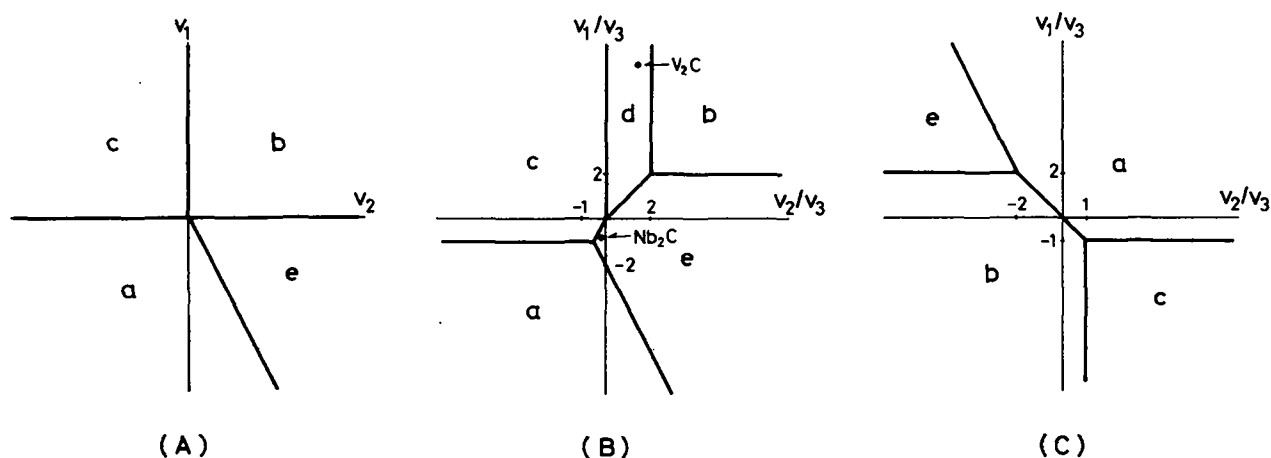

(A)   **(B)**   **(C)**

FIG. 3. — Existence regions of the five structure types of M₂X. (A) $v_3 = 0$, (B) $v_3 > 0$, (C) $v_3 < 0$. The data of v_1/v_3 and v_2/v_3 estimated for V₂C and Nb₂C are plotted in (B).
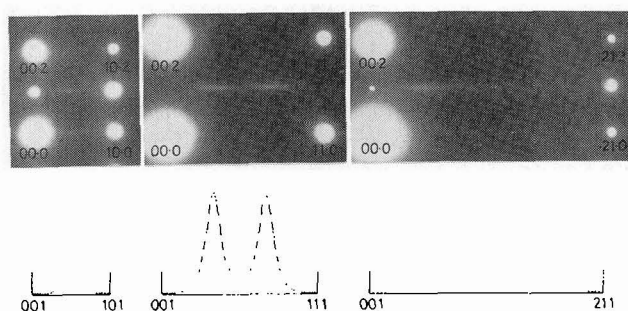
FIG. 4. — Electron diffraction patterns of V_2C quenched from 1 200 °C. The patterns A, B and C correspond to the reciprocal lattice planes of $k = 0$ with [01.0] incidence, $h = k$ with [1$\bar{1}$.1] incidence, and $h = 2k$ with [$\bar{1}$2.0] incidence, respectively. Dotted curves are $I(k)$ calculated with $v_1/v_3 = 7$, $v_2/v_3 = 1.5$ ($v_3 > 0$) and $T_c/T = 0.95$.
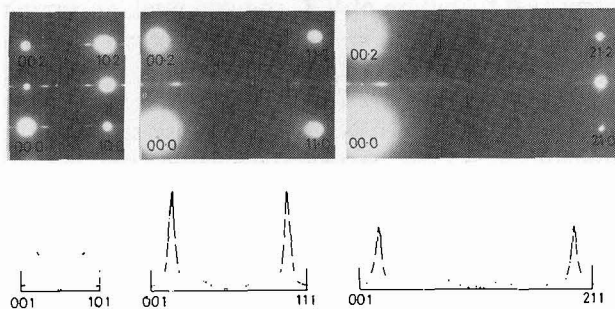

FIG. 5. — Electron diffraction patterns of Nb_2C quenched from 1 600 °C. The orientation for each pattern is identical with figure 4. Dotted curves are $I(k)$ calculated with $v_1/v_3 = -0.8$, $v_2/v_3 = -0.2$ ($v_3 > 0$) and $T_c/T = 0.95$.

Hence the short-range ordered structures of the quenched specimens are described as two dimensional

correlations of the C-v rows. The intensity distribution of diffuse scattering is given by the formula [7]

$$I(k) = \cfrac{c}{1 - \cfrac{T_c}{T} \cfrac{v(k)}{v(k_m)}}, \qquad (3)$$

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 $(V_x Nb_{1-x})_2C$. 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 ζ-Fe_2N and anti-$CaCl_2$ types in figure 2(B). Similar studies of $(Nb_x Ta_{1-x})_2C$ and $(V_x Ta_{1-x})_2C$ are now in progress.

4. Conclusion. — The existence conditions of the five ordered structures of hcp Hägg compounds M_2X were determined as functions of the pair-wise interactions between the interstitial atom rows up to the third neighbors. The electron diffraction study on $(V_x Nb_{1-x})_2C$ quenched from 1 200-1 600 °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.

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