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SUBSTITUTING ATOMS  
IN CRYSTALS OF SOLID  
SOLUTIONS FORMED  
BY INTERMETALLIC  
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CRYSTALLOGRAPHY

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## Abstract

## Full Text

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CRYSTALLOGRAPHY

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# THE FACTOR OF CHEMICAL INDIFFERENCE OF MUTUALLY SUBSTITUTING ATOMS IN CRYSTALS OF SOLID SOLUTIONS FORMED BY INTERMETALLIC COMPOUNDS

*(Presented by Academician A. P. Vinogradov on 25 VII 1968)*

The concepts now prevailing concerning the causes of isomorphous mutual substitution of atoms in crystals of solid solutions are based on three factors of similarity of the components: a) similarity of chemical nature, b) similarity of crystal structure, and c) similarity of the sizes of atoms (ions). However, the large number of exceptions leads to the supposition that there exists a more fundamental factor determining the possibility of isomorphous mutual substitution of atoms of different chemical elements in structurally equivalent positions of solid-solution crystals. Such a factor is <sup>(1)</sup> the mutual chemical indifference of the atoms occupying a given set of equivalent positions of the crystal structure.

The assumption that this factor exists followed from general considerations in contrasting the physical essence of chemical compounds and solid solutions as mixtures of components. Indeed, the presence of forces of chemical interaction between atoms of different elements leads to the formation of compounds, while their absence, i.e., chemical indifference, determines the possibility of mixing atoms or "molecules" \* of different compounds in the crystal structure of a solid solution. For the crystalline state, the mixing of atoms or "molecules" in the formation of a solid solution means a statistically disordered distribution of atoms (ions) of different elements in one and the same set of equivalent positions of the structure. The structural-geometrical aspects of the crystal structure of compounds and solid solutions are considered in more detail in work <sup>(2)</sup>.

It follows from this that complete isomorphism (perfect isomorphism), i.e., the formation of a continuous series of solid solutions by two or several substances, is controlled first of all by the factor of mutual chemical indifference. But its action may be limited by the influence of an unfavorable ratio of the sizes of the mutually substituting particles in the given structure, as well as by thermodynamic factors of equilibrium, into the consideration of which we shall not enter

here.

The experimental criteria of mutual chemical indifference of the atoms or ions of two elements are the phase diagrams of their binary systems of the following five types: a) with immiscibility in the liquid and solid states; b) of the eutectic or peritectic type; c) with a continuous series of solid solutions; d) with very wide regions of solid solutions at both components of the system and a narrow two-phase region between them (for example, as in the lithium–magnesium system); e) with a broad ( $\geq 20$  at.%) region of solid solutions at one of the components—usually a transition metal (for example, as in the iron–aluminum system).

\* What is meant here is not molecular solid solutions, but atomic (ionic) ones, where discrete molecules are absent in the crystals.

As Yu. A. Pyatenko has already noted earlier (<sup>3</sup>), the concept of isomorphism should at present be applied not to crystals, but to atoms, since the phenomenon of isomorphism is based on the mutual substitution of atoms, or of their derivatives—ions—in crystals. In the old classical understanding, the word isomorphism denotes the equal-shapedness of the crystals of the initial components and of their isomorphous mixtures—mixed crystals. In the modern understanding, the word isomorphism does not lose its literal meaning, if one has in mind not so much the identity of the external form of crystals as the identity of the internal form of location—the coordination and interatomic distances—of atoms of different elements in structurally equivalent positions of crystals of solid solutions. Identity of external form and isostructurality, as well as similarity in the chemical nature of the elements whose atoms or ions enter into isomorphous relations with one another in the crystals of minerals and compounds, are by no means obligatory. For example, such pairs of elements as magnesium and iron, lithium and iron, aluminum and silicon, calcium and uranium, etc., are not isostructural and are very different in chemical nature; nevertheless, their ions possess complete, or very broad, isomorphous mutual substitutability in many minerals and compounds (<sup>1</sup>, <sup>2</sup>). On the other hand, for example, silver and copper, zinc and cadmium are isostructural, but do not form continuous series of solid solutions with one another; this, however, does not prevent them from being isomorphously mutually substitutable in many continuous series of solid solutions of their compounds with other elements. All the indicated pairs of elements are chemically mutually indifferent, and this is the main criterion determining the isomorphous mutual substitutability of their ions in solid solutions of the corresponding compounds. In mineral objects, as shown in (<sup>1</sup>), this criterion, given favorable ratios of ion sizes, is fulfilled without exception.

It should be expected that in the formation of solid solutions of intermetallic compounds the criterion of mutual chemical indifference will also be fulfilled, especially in those cases where the influence of the heteropolar component of the bond is significant. Analysis of the experimental material contained in the extensive review (<sup>4</sup>) fully confirms this. According to the data of this review, Table 1 gives systems of continuous solid solutions only for those intermetallics whose mutually substituting atoms belong to elements that do not form contin-

uous solid solutions with one another and in most cases are not isostructural. We have not included in Table 1 the numerous systems of continuous intermetallic solid solutions whose mutually substituting elements, in the state of simple substances, are isostructural and form continuous series of solid solutions with one another, as trivial and entirely understandable cases. For the systems of solid solutions presented in the table, it is evident that the atoms mutually substituting in these systems are chemically quite mutually indifferent and, in the elemental state, give melting diagrams: (a) with immiscibility in the liquid and solid states, (b) of the eutectic (peritectic) type, or (c) with broad regions of solid solutions.

Thus, the criterion of mutual chemical indifference encompasses and explains from a unified point of view the entire diversity of combinations of mutually substituting elements in the crystals of continuous substitutional solid solutions having an atomic structure. To the same extent that the factor of chemical interaction is the cause of the formation of chemical compounds, the factor of mutual chemical indifference is responsible for the formation of solid solutions or for the immiscibility of simple substances with one another and of chemical compounds with one another.

It should be noted that the weak chemical affinity manifested in the formation of ordering phases in many systems of solid solutions of elemental simple substances at low temperatures does not diminish the role of the factor of chemical indifference and does not serve as an obstacle to isomorphous

Table 1

Continuous series of solid solutions	Types of crystal structure	Mutually substituting elements and type of their phase diagram
AlAs–InAsAlSb–InSb	Sphalerite	Al–Immiscibility gap
AlAs–GaAsAlSb–GaSb	Sphalerite	Al–Gaeutectic
GaSb–InSbGaAs–InAs	Sphalerite	Ga–Ineutectic
ZnS–CdSZnTe–CdTe	Sphalerite	Cd–Zneutectic
CdTe–InTeCdSb–InSb	Sphalerite, TlSe	Cd–Ineutectic
CdTe–HgTe	Sphalerite	Cd–Hgwide series of solid solutions
GeTe–SnTe	NaCl	Ge–Sneutectic
PtBi–PtPb	NiAs	Bi–Pbwide series of solid solutions
Mo <sub>3</sub> Al–Mo <sub>3</sub> SiZr <sub>5</sub> Al <sub>3</sub> –Zr <sub>5</sub> Si <sub>3</sub> Zr <sub>2</sub> Al–Zr <sub>2</sub> Si	$\beta$ -WMn <sub>5</sub> Si <sub>3</sub> CuAl <sub>2</sub>	Al–Sieutectic
Ti <sub>3</sub> Al–Ti <sub>3</sub> SnNi <sub>3</sub> Al–Ni <sub>3</sub> Sn	Mg <sub>3</sub> Cd	Al–Sneutectic
Ni <sub>3</sub> Sn–Ni <sub>3</sub> In	Mg <sub>3</sub> Cd	In–Snwide series of solid solutions

Continuous series of solid solutions	Types of crystal structure	Mutually substituting elements and type of their phase diagram
AgZn–CuZnAg <sub>5</sub> Zn <sub>8</sub> – Cu <sub>5</sub> Zn <sub>8</sub> AgZn <sub>3</sub> –CuZn <sub>3</sub>	$\beta$ -brass $\gamma$ -brass $\delta$ -brass	Ag–Cu eutectic
AgZn <sub>3</sub> –MnZn <sub>7</sub>	$\delta$ -brass	Ag–Mn wide series of solid solutions and miscibility gap
Cu <sub>5</sub> Zn <sub>8</sub> –Cu <sub>9</sub> Al <sub>4</sub> AgZn <sub>3</sub> – Ag <sub>3</sub> Al <sub>3</sub>	$\gamma$ -brass $\delta$ -brass	Al–Zn eutectic and wide series of solid solutions

of atomic mutual substitutability in solid solutions. The reason for the formation of ordered structures of solid solutions is not so much chemical as physical: as a result of the leveling of local stresses arising from differences in the sizes and other characteristics of atoms, an ordered structure, compared with a disordered one, is energetically more favorable. The category of weak chemism, which does not prevent isomorphism, should apparently also include interactions of a purely metallic character, leading to the formation of the most typical intermetallic structures, for example Laves phases (KNa<sub>2</sub>), berthollide phases in the magnesium–aluminum system, etc.

The construction of a quantitative theory for determining the limits of isomorphic mutual substitutability of atoms in crystals, taking into account the influence of chemism and bond type on the degree of mutual indifference of atoms of different elements in their various combinations and under various physicochemical conditions (temperature, pressure, concentration), requires further research. An assessment of the role of the factor of mutual chemical indifference in the formation of limited  $\alpha$ -solid solutions, intermediate intermetallic phases of variable composition, and phases built according to the principle of changing the number of atoms in the unit cell will be made in a separate article.

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*Note: Figure translations are in progress. See original paper for figures.*

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