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Nonstoichiometry in the $ZrSe_2$ Phase

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Nonstoichiometric $ZrSe_2$ phase characterized by a C6 structure type has been studied on compounds prepared at 800° by direct synthesis. The limits of the homogeneous phase, determined from lattice constant measurements, are related to Se/Zr = 1.850 and Se/Zr = 1.945 atomic ratios. For the highest selenium content, the crystal contains selenium vacancies. As Se/Zr decreases, zirconium additional atoms occupy these vacancies. When they are all filled up, the lowest selenium limit is reached. Lattice constant variations are interpreted through this model.

Introduction

A large number of transition metals, when combined with chalcogens, give nonstoichiometric compounds. In the particular case of Column IV transition metals, all dichalcogenides, which crystallize in C6-CdI_2 type, exhibit large deviations from stoichiometry, the extent of which strongly changes from one compound to another. Zirconium diselenide, one of those compounds, has been first synthetized by Van Arkel (*1*), who has found for it the C6 type structure. As the other members of that family, it shows a nonstoichiometric behavior which has been simultaneously and independently described by MacTaggart and Wadsley (*2*) and by Hahn and Ness (*3*, *4*). MacTaggart and Wadsley obtained by thermal decomposition of zirconium triselenide a compound of formula $ZrSe_{1.95}$. Hahn and Ness have reported, synthetizing directly compounds at 800°, the existence of a broad homogeneous phase limits of which are defined by Se/Zr = 2 and Se/Zr = 1.7 ratios.

Undertaking a crystallochemical study of the ternary (Zr, Se, Te) system, it has appeared to us necessary to study again the $ZrSe_2$ nonstoichiometric phase, when the temperature of preparation is 800°.

Experimental

Diselenides have been prepared by direct synthesis starting from powdered zirconium (100 mesh; 99.5% purity) and from powdered selenium (99.8% purity) which react in vacuum sealed silica tubes. Compositions, indicated by the ratio n = (Se atom number)/(Zr atom number), are determined by weighing the elements with an average relative error of 0.15%. Samples made correspond to n values ranging from 1.70 to 2.05.

Preliminary experiments have pointed out that the crude use of silica vessels leads to a noticeable change of composition because interfering reaction between zirconium and silica occurs. In order to avoid this trouble, the elements are put in a small sintered alumina crucible which is introduced into the silica tube. The latter is evacuated before sealing using a mercury diffusion pump associated to a liquid nitrogen trap; residual pressure is considered to be *circa* 10^{-4} Torr.

In order to get homogeneous compounds which, moreover, must be in thermodynamic equilibrium, it has appeared necessary to make the thermal treatment in two steps. First of all, a heating at 500° for 2 days allows the reaction of zirconium with selenium; the sample is then heated at 800° during 8 days. Selenides, as shown by X-rays, are not homogeneous. In the second step, they are carefully powdered and heated a second time at 800° for 3 weeks and finally water quenched.

Diselenides appear as dark, bronze-green, microcrystalline powders without any single crystals.

Regarding the preceding remark about interfering zirconium-silica reaction, it has been considered useful to check compositions after synthesis by roasting selenides in flowing air at 1000°. In most cases, Se/Zr ratios given by chemical analysis (with an error of 0.4%) do not differ from those known by weighing by more than 0.5%.

Homogeneity of prepared compounds is controlled through X-rays using a Seeman–Bohlin camera associated to a monochromator set for CuKα radiation. The examination of photographs proves the existence of a nonstoichiometric phase: For Se/Zr ratios ranging from 1.85 to 1.95, all diffraction lines are those of the C6 type. If Se/Zr ratio is greater than 1.95, X-ray photographs show that zirconium triselenide is present. Below $n = 1.85$, the appearance of additional lines of which the intensity grows with a decrease of n, proves that compounds belong to a two-phased region. These additional lines are characteristic of Zr_3Se_4 which is rhombohedral (*5*).

Thus from a qualitative point of view, limits of the homogeneous nonstoichiometric phase are Se/Zr = 1.85 and Se/Zr = 1.95. The lower limit is quite different from the one proposed by Hahn and Ness, found at 1.7 by these authors. In order to give more accurate limits and to determine the nature of defects responsible for nonstoichiometry, measurements of lattice constants and of density have been carried out.

Values of Bragg angles recorded with a Siemens diffractometer have been treated by a least squares method to get lattice constants. Radiation was nonmonochromatized CuKα. The sample carefully powdered was mixed with a silicon grease and the obtained paste was spread out on a glass plate as a regular layer of 0.1 mm-thickness. The sample holder and the counter turned on the θ–2θ mode and line profiles were recorded following step scanning. The step was equal to 0.02° for Bragg angles lower than 35° and to 0.05° for Bragg angles going from 35° up to 75°. Mechanical zero has been checked for every sample recording a few lines on both sides of zero.

The least squares method is the classical one used to compute lattice constants from Debye and Scherrer diffractograms (*6*, *7*). In Bragg law, $\sin^2\theta$ may be written as:

$$\sin^2\theta = \sin^2(\theta_M + \Delta\theta_M) + \epsilon$$

The term θ_M is measured angle, and $\Delta\theta_M$ is systematic error which has three chief reasons: absorption, sample flatness, and beam divergence. The term, ϵ is the error due to measurement error.

Wilson (*8*) and Eastabrook (*9*) have evaluated $\Delta\theta_M$. They proposed an equation which may be simplified in the present case, since absorption is important:

$$\Delta\theta_M = -m\cdot\sin 2\theta_M - n\cdot\operatorname{cotg} 2\theta_M,$$

where m and n are two positive constants which depend on absorption coefficient, sample geometry and diffractometer radius. Theoretically this relation is only valid if θ_M is related to the line center. However it may be used with θ_M being the angle of the profile maximum (*10*). Thus $\sin^2\theta$ may be developed and reported in Bragg relation:

$$\epsilon = \frac{\lambda^2}{3a^2}(h^2 + hk + k^2) + \frac{\lambda^2}{4c^2}l^2 - \sin^2\theta_M + $$
$$+ m\cdot\sin^2 2\theta_M + n\cdot\cos 2\theta_M$$

There are four unknown values: $1/a^2$, $1/c^2$, m and n.

About 20 $K\alpha_1$ lines and 10 $K\alpha_2$ lines have been recorded for every sample. In order to take account of errors made by determining Bragg angles, errors dependent on Bragg angle values and on intensity, measured values have been weighted in least squares computation. A line of Bragg angle θ and of observed height h was weighted by a factor $h\cdot\mathrm{tg}\theta$. For a $K\alpha_2$ line, the weighing factor has been multiplied by $h_1/2h_2$ to take account of variable resolution of $K\alpha_1 - K\alpha_2$ doublet; the weight then is $[h_2\mathrm{tg}\theta_2]$ $[h_1/2h_2]$. Indeed $h_1/2h_2$ is not equal in fact to one since $K\alpha_1 - K\alpha_2$ separation has not been done.

Standard deviations, computed following Cox's progam (*11*), are of the order of 3.10^{-4} Å for a parameter and 7.10^{-4} Å for c parameter. Experimental results are gathered in Table 1.

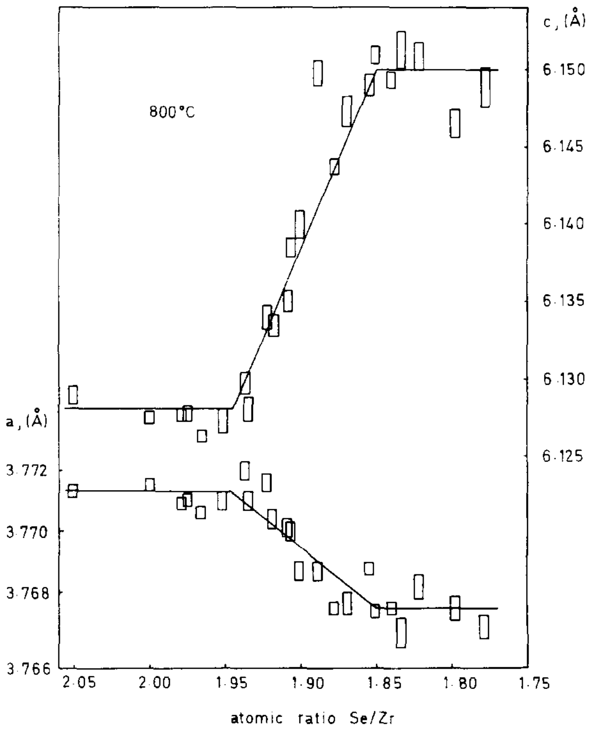

FIG. 1. Lattice constants variations as a function of composition.

Lattice constant variations are shown by Fig. 1. Note that *a* decreases and *c* increases as Se/Zr ratio changes from 1.945 to 1.850. These two values, abscissas of observed discontinuities, are taken as limits of the $ZrSe_2$ nonstoichiometric phase, which confirms qualitatively results described above.

To measure densities of powdered zirconium selenides, we have used hydrostatic methods. Experimental technics and cares have been previously described elsewhere (*12*). Let us just point out that powders have been set under vacuum during 6 hr before been immersed in liquid, which is 1-1-2-2-tetrabromoethane. Measurements have been carried out on about 6*dg* selenides and the error then is close to 0.3%. There are collected in Table I results related to seven compounds of the phase, chosen from among those whose lattice constants have been measured.

The variation of the unit-cell mass computed from densities and lattice constant measurements is plotted on Fig. 2 as a function of composition. The three theoretical curves related to the three elementary types of defects are shown together on this figure: selenium vacancies, substitution of selenium by zirconium, and zirconium additional atoms.

TABLE I

VALUES OF LATTICE CONSTANTS AND DENSITIES

n = Se/Zr	a (Å)	c (Å)	Density (g/cm³)	Mass of the unit cell
Out of Phase				
2.051	3.7713	6.1289		
2.000	3.7715	6.1275		
1.979	3.7709	6.1276		
1.975	3.7710	6.1277		
1.966	3.7706	6.1262		
1.952	3.7710	6.1272		
Homogeneity Range				
1.937	3.7720	6.1297		
1.935	3.7710	6.1280	5.372	244.2
1.923	3.7716	6.1339	5.377	244.8
1.919	3.7704	6.1334		
1.909	3.7702	6.1349		
1.907	3.7701	6.1384	5.377	244.8
1.901	3.7687	6.1399	5.394	245.4
1.889	3.7687	6.1498	5.442	248.0
1.878	3.7675	6.1437		
1.870	3.7676	6.1473	5.426	247.0
1.855	3.7688	6.1490	5.449	248.3
1.851	3.7674	6.1510		
Out of Phase				
1.840	3.7675	6.1494		
1.834	3.7667	6.1513		
1.822	3.7682	6.1509		
1.779	3.7669	6.1489		

Discussion

First of all, it must be pointed out that stoichiometric $ZrSe_2$ zirconium diselenide cannot be prepared at 800°. Indeed the compound of highest selenium content is $ZrSe_{1.945}$. This result is in good agreement with the one of MacTaggart and Wadsley (*2*), although the preparation mode is not the same. Concerning this particular compound, the determination of the unit-cell mass leads to the conclusion that the lattice contains selenium vacancies at an average concentration of $2 - 1.945 = 0.055$ per unit cell.

If now the selenium lowest limit is considered, Fig. 2 shows that the unit-cell mass may be related to a substitution of selenium atoms by zirconium atoms.

As the Se/Zr ratio decreases from the 1.945 highest value, the unit-cell mass continuously increases. This fact may be understood considering that zirconium atoms, as they enter into the lattice, occupy empty selenium sites. This mechanism leads to the following general formula

$$Zr_1\ Zr(Se)_{\alpha}\ Se_{1.945}\ Se_{0.055-\alpha},$$

for the nonstoichiometric phase. Assuming this mechanism, a theoretical curve may be calculated starting from the selenium-deficient compound corresponding to $n = 1.945$. Thus, the limit of the phase which occurs when all vacancies are occupied by zirconium, is given by the intersection of this dashed line (Fig. 2) with the substitution line. The abscissa of that point is $n = 1.844$, which is in very good agreement with the $n = 1.850$ experimental value, within experimental errors. Thus it appears reasonable to accept the proposed model in as much as experimental points chosen inside the phase are fairly well located on that computed line.

Now the nature of defects is known, an interpretation of the observed variations of lattice constants as a function of composition may be proposed, although the nature of the chemical bond cannot be precisely described.

The C6 structure, in which the studied selenides crystallize, is made of the stacking of metal and nonmetal planes in the sequence...Se–Zr–Se–Se–Zr–Se.... In the unit cell, zirconium is at the origin

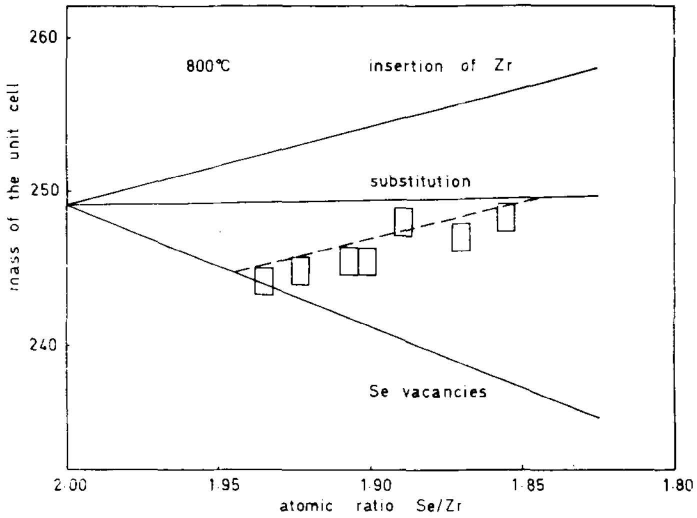

FIG. 2. Determination of defects responsible of nonstoichiometry in $ZrSe_2$ homogeneous phase; rectangles are experimental points.

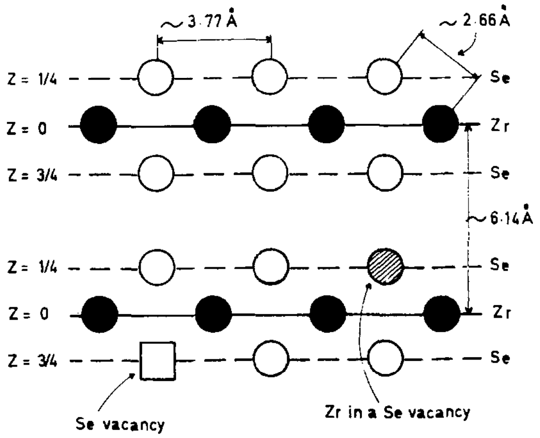

FIG. 3. C6 type lattice: projection on the (100) plane showing defects in $ZrSe_2$.

while selenium atoms occupy equivalent sites (1/3, 2/3, z) and (2/3; 1/3, $\bar{z}$), with z close to 1/4, a value close to that found for other C6 compounds, (*12*, *13*) (Fig. 3).

The bond length Zr–Se, which binds a Zr atom of the $z = 0$ plane to a Se atom of the $z = 1/4$ plane, is equal to 2.66 Å. Between a Zr atom located in the $z = 1/4$ plane and its selenium neighbour of the same plane, the distance is much larger, being equal to 3.77 Å. The chemical bond cannot be accepted as purely ionic (metallic lustre), which means that this zirconium atom is not in a very different state from those of the $z = 0$ plane. Therefore such a bond Zr–Se in a plane $z = 1/4$ or $z = 3/4$ must exhibit a tendency to be much shorter than 3.77 Å; this leads to a shortening of this value, that is of the a axis, as much as the amount of additional atoms Zr is larger.

Additional zirconium atoms located in the $z = 1/4$ or 3/4 planes present contacts with zirconium atoms of the $z = 0$ plane. In nonstoichiometric titanium disulfides (*12*), the nature of defects is different since additional Ti atoms are located in the $z = 1/2$ plane. However Ti–Ti contacts occur and interatomic distances are quite similar to those observed for the metal. It may be accepted that the chemical bonds in $ZrSe_2$ and TiS_2 are not too different. Therefore considering that the Zr–Zr distance in the metal is 3.18 Å for the hexagonal form and 3.13 Å for the cubic form (*14*), and assuming $z = 1/4$ again, distortion must be high since the Zr–Zr distance observed between one Zr atom of the $z = 0$ plane and one Zr atom of the $z = 1/4$ plane is 2.67 Å. This may be presented as an explanation for the increase of the c axis with the decrease of n ratio, that is, with the number of Zr atoms located in the $z = 1/4$ or $z = 3/4$ planes.

Conclusion

The most commonly met defect mechanism for C6 compounds corresponds to a metal insertion in the $z = 1/2$ plane. Examples are cobalt ditelluride (*17*) and titanium disulfide (*12*). Another type of nonstoichiometry of the vacancy type has been met recently for compounds of structure related to the C6 type. They are molybdenum diselenide and ditelluride which crystallize in the molybdenumsulfide type and which contain chalcogen vacancies (*15*).

In the present study, the situation appears more complicated since two defect types simultaneously occur. The selenium-richest compound contains only selenium vacancies. However, as the Se/Zr ratio decreases, vacancies continuously disappear since additional zirconium atoms fill them up. Phase limit is reached when all selenium vacancies are occupied.

Such complex mechanisms have been already met for more complicated systems such as calcium stabilized zirconia (*16*). However, comparison between this mixed oxide and zirconium diselenide looks difficult since many features, such as the chemical bond, are too different.

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