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The Crystal Structure of $RhSe_2$

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The crystal structure of $RhSe_2$ has been determined from X-ray powder diffraction data. $RhSe_2$ has the pyrite-type structure (*C*2 of the *Strukturbericht*). Four rhodium atoms are in positions 4(*a*): $(0, 0, 0; 0, \frac{1}{2}, \frac{1}{2}; \circlearrowleft)$ and eight selenium atoms in positions 8(*c*): $\pm(x, x, x; \frac{1}{2}+x, \frac{1}{2}-x, \bar{x}; \circlearrowleft)$ of space group $T_h^6\text{–}Pa3$, with $x = 0{\cdot}380\pm0{\cdot}002$.

A homogeneity range exists for the structure between about 60 and 71·4 atomic % selenium with a decrease in lattice constant with increasing selenium content.

Introduction

In the study of superconductivity of intermetallic systems in these Laboratories, many binary rhodium compounds have been investigated (Matthias, 1953, 1954; Geller & Wood, 1954; Geller, 1955). The rhodium–selenium system is one of those in which superconductivity exists.

Original work on the rhodium–selenium system by Wöhler, Ewald & Krall (1933) led them to the conclusion that only a phase of composition Rh_2Se_5 existed in the system. These authors prepared their compound by first heating the chloride with an excess of selenium in a stream of CO_2 at 600° C. to bring about reaction, following which additional selenium was added; the mixture was then sealed in an evacuated tube and again heated to 600° C.

Later work by Biltz (1937) corroborated that of Wöhler *et al.* Biltz prepared Rh_2Se_5 in a manner similar to that described by Wöhler. Moreover, Biltz took X-ray powder photographs of the Rh_2Se_5 and concluded that it had a pseudo-pyrite structure. He stated that he observed definite line-splitting around line positions of a pyrite-type (*Strukturbericht*, 1931) structure.

The rhodium–selenium preparations to be discussed were obtained from B. T. Matthias. The samples were prepared by mixing rhodium and selenium in definite proportions, sealing the mixture in a fused silica tube and heating to 900° C. for 1–3 days. The range 40–71·4 atomic % selenium was investigated. X-ray powder photographs indicated the existence of two rhodium–selenium phases in this range, at least one of which has an Se:Rh ratio greater than 1. Because the photograph of the 40 atomic % preparations showed the presence of excess rhodium, it is probable that no new Rh–Se phase (other than that seen in the 40 atomic % photograph) appears in the 0–40 atomic % range. No composition in the range 54·6 < atomic % Se < 60 was made. The more rhodium-rich phase was still fairly strong in the photograph of the 60 atomic % Se composition. Traces of this phase were also seen in the photograph of the 63·6 % composition. Our main interest is in the selenium-rich phase, which, it will be shown, has the pyrite-type structure (*C*2). It will also be shown how the work done by Wöhler and by Biltz could have led to incorrect results.

Determination of the structure

Powder diffraction photographs were taken of preparations containing 40, 50, 54·6, 60, 63·6, 66·7, 68·6 and 71·4 atomic % Se. The Se-rich phase first appeared in the preparation containing 60 atomic % Se; it was very strong in the 63·6 atomic % Se photograph.

The photographs of the 66·7, 68·6 and 71·4 atomic % Se showed a pure phase. The lines of these powder photographs were indexed on a cubic cell with lattice constants $a = 6{\cdot}002$, 5·991, and 5·985 Å (all ±0·002 Å) respectively. Reflections of the type (0*kl*), *k* odd, are absent, leading to $T_h^6\text{–}Pa3$ uniquely as the space group. Assuming 4 $RhSe_2$ in the unit cell, the X-ray density of $RhSe_2$ is 8·012 g.cm.$^{-3}$, in excellent agreement with the value determined pycnometrically (8·03 g.cm.$^{-3}$).

The structure was determined from X-ray data obtained with the Norelco diffractometer. The new specimen spinner which rotates a circular disc sample in the plane of the circle was used. The radiation used was Cu $K\alpha$ (Ni filtered). The data were recorded on charts, and relative integrated intensities were obtained with a Keuffel and Esser compensating polar planimeter. The single Se parameter which gives extremely good agreement (see Fig. 1) between calculated and observed intensities for all but the three strongest reflections is 0·380. This value is probably good to within ±0·002 on the basis of changes occurring in intensities for different parameter values, and gives the same Se–Se distance in $RhSe_2$ as exists in $CoSe_2$ (Lewis & Elliot, 1940), namely 2·50 Å. This is appreciably greater than the elementary Se–Se distance, 2·32 Å (see Lewis & Elliot, 1940).

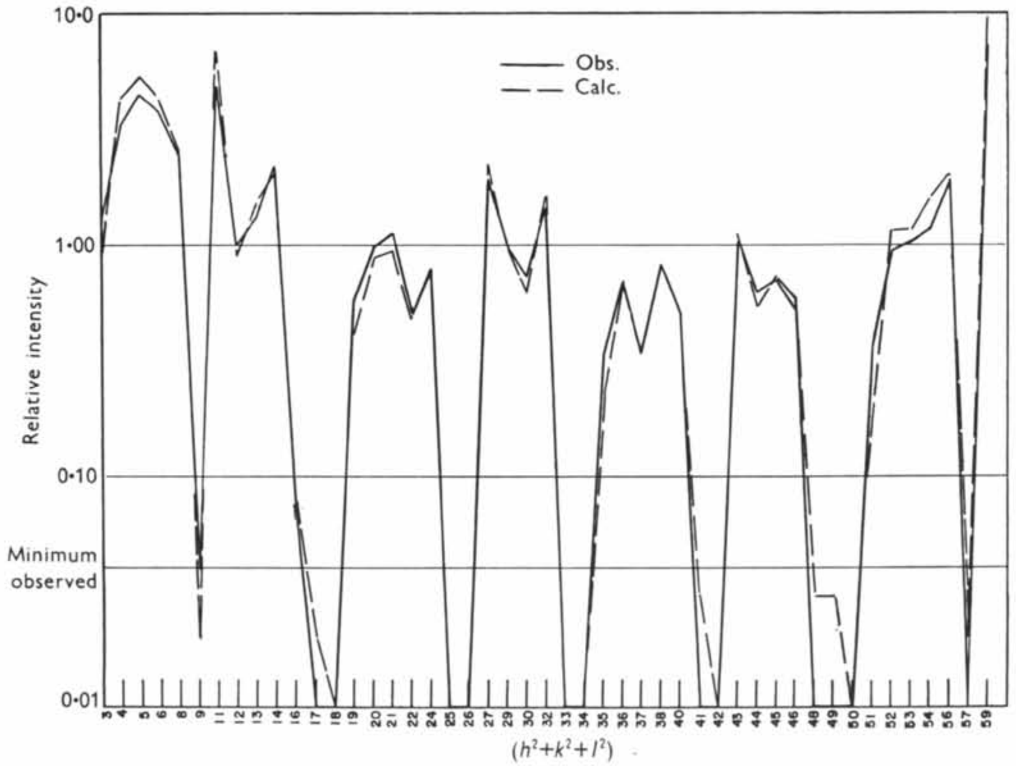

Fig. 1. Comparison of calculated with observed intensities.

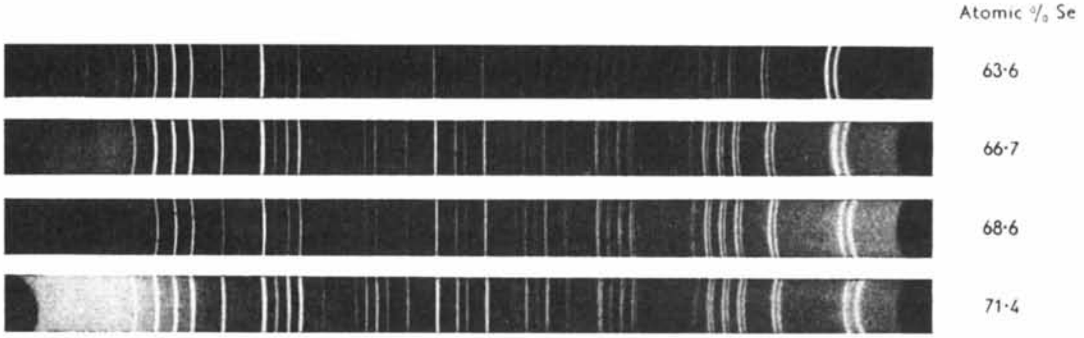

Fig. 2. Homogeneity range in $RhSe_2$.

Homogeneity range in $RhSe_2$

The whole phase diagram of the rhodium–selenium system was by no means investigated but enough has been done to enable us to draw some interesting conclusions. It is first of all obvious that $RhSe_2$ will dissolve either rhodium or selenium. This may be seen vividly in Fig. 2. The four powder photographs are those of the 63·6, 66·7, 68·6 and 71·4 atomic% Se preparations. The lattice constants of the $RhSe_2$ phase in each were 6·015, 6·002, 5·991, 5·985 Å (all ±0·002 Å) respectively. The last three were pure phases; the first contained a very small amount of a more rhodium-rich phase. Thus, with additional rhodium the cell gets larger and with addition of selenium the cell gets smaller.

Because the more rhodium-rich solution indicated the presence of a small quantity of another phase, no density measurements were made on it. The following discussion will therefore be concerned only with solutions of selenium in $RhSe_2$.

One can make three simple hypotheses concerning these solutions:

1. The Se atoms replace Rh atoms. This would decrease the density and probably the lattice constant.
2. The Se atoms create Rh vacancies. This would decrease the density and probably also the lattice constant.
3. The Se atoms go into the crystal interstitially.

This would increase the density and probably the lattice constant.

There could, of course, be combinations of these which cannot be settled by density measurements alone. X-ray intensity measurements, other than perhaps the most careful absolute ones, will not distinguish between the first two. And perhaps diffuse scattering measurements might yield some information regarding the third.

Listed in Table 1 are the values calculated for the various hypotheses and also the pycnometrically determined values.

Table 1. *Densities of* $RhSe_2$ *solutions of* Se *under three hypotheses*

Atomic % Se*	Rh vacancies	Rh replacement	Interstitial	Measured†
66·7	8·01 g.cm.$^{-3}$	8·01 g.cm.$^{-3}$	8·01 g.cm.$^{-3}$	8·03 g.cm.$^{-3}$
68·6	7·77	7·99	8·13	7·80
71·4	7·44	7·93	8·34	7·93

* These are the amounts used in the reaction mixture.

† Density measurements on samples from each of these preparations are reproducible to ±1%.

The best case for comparison is that with 71·4 atomic % Se. The results indicate that a pure vacancy situation is impossible in this case, so that either a replacement of the Rh atoms occurs or some combination of the three possibilities. (The pure interstitial situation is ruled out mainly by space considerations.)*

Discussion

The pyrite or *C*2-type structure has been very adequately described in the *Strukturbericht* (1931). It will suffice then to report briefly the coordination and interatomic distances in $RhSe_2$. These are shown in Table 2.

Table 2. *Interatomic distances in* $RhSe_2$

Atom	Number of equivalent neighbors	Neighboring atom	Distance (Å)
Rh	6	Se	2·50
Rh	6	Se	3·85
Rh	2	Se	3·95
Rh	12	Rh	4·24
Se	1	Se	2·50
Se	3	Rh	2·50
Se	3	Se	3·38
Se	3	Se	3·68
Se	3	Rh	3·86
Se	1	Rh	3·95

It was mentioned earlier that previous investigators reported the existence of the compound Rh_2Se_5. The method of preparation used by these investigators may not have yielded pure phases. If failure to attain equilibrium resulted in the formation of a mixture of solid solutions of Rh or Se (or both) in $RhSe_2$, a powder photograph with apparent line splitting would be obtained. This may be seen from an examination of Fig. 2. Also the density of $RhSe_{2.45}$ reported by Biltz (6·96 g.cm.$^{-3}$) is quite low, which may be an indication of incomplete reaction and the presence of some free selenium.

The authors wish to thank Dr B. T. Matthias for his interest in this problem and Mr E. Corenzwit, who took the powder photographs.

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* All important errors in pycnometric density measurements of solids cause reduced values. Undissolved selenium or silica fragments from the reaction vessel, if present, would also cause low values. Thus one may not assert that possibilities for which the theoretical is higher than the measured density should be ruled out. The 68·6 atomic % Se case is not favorable for interpretation because of the small differences, but is included to indicate trend.

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