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Neutron and X-ray Diffraction Study of LiRh*

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A study of the crystal structure of LiRh was made by combined neutron and X-ray diffraction techniques to determine unambiguously the positions of lithium atoms in the unit cell. The unit cell is hexagonal; space group $P\bar{6}$; $a_0 = 2{\cdot}649 \pm 0{\cdot}003$, $c_0 = 4{\cdot}357 \pm 0{\cdot}002$ Å, with one Rh at (0,0,0) and one Li at ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{2}$) and calculated density $\varrho = 6{\cdot}88$ g.cm^{-3}. Rh atoms are in one layer and Li in the other, the layers alternating along the c axis at $c_0/2$ distance apart. The interatomic distances are Rh–Rh = 2·649, Li–Li = 2·649 and Rh–Li = 2·663 Å.

Introduction

Lithium and rhodium form a Li–Rh binary alloy at approximately 1 to 1 molar ratio. The X-ray scattering by lithium is small compared with that of rhodium but the coherent nuclear scattering amplitudes of the two nuclei for thermal neutrons are comparable. It seemed feasible, therefore, to investigate the alloy by the combined neutron and X-ray diffraction techniques and determine unambiguously the positions of lithium atoms in the structure. In this paper are given the preparation and the crystal structure determination of this alloy.

Experimental Procedure

The LiRh sample was prepared from high purity polycrystalline rhodium, and lithium isotope 7. The use of ^{7}Li was made in order to take advantage of its higher coherent scattering amplitude as compared with that of natural lithium. Rhodium metal was rolled to about 2 mil thick foil which was cut into small pieces and mixed with small pieces of lithium. The amount of lithium in the mixture was about 25 atomic per cent in excess of 1 to 1 molar ratio of the metals. The mixture was packed into an iron crucible and placed in a Vycor tube. The crucible was covered with a lid to prevent lithium from evaporating into the tubing and reacting with it. The mixture was heated to 750–800 °C under dry argon atmosphere for an hour. The tubing was then removed from the furnace and allowed to cool in air. The alloy had shiny metallic lustre and was brittle as compared with ductile rhodium. The X-ray diffraction pattern of the specimen did not indicate the presence of any impurity.

Results

X-ray and neutron diffraction patterns of LiRh alloy are shown in Fig. 1 and the diffraction data are given in Table 1. A hexagonal structure was derived from these data and was employed to obtain the following structure constants.

Table 1. *Interplanar spacings (d), calculated and observed X-ray and neutron diffraction intensities (I/I_0) for* LiRh

		X-rays		Neutrons	
hkl	*d*	I/I_0(calc)	I/I_0(obs)	I/I_0(calc)	I/I_0(obs)
001	4·36 Å	100·0	*vs*	100·0	100·0
100	2·29	57·7	*s*	68·2	60·7
002	2·18	19·1	*m*	5·8	12·3
101	2·03	88·3	*vs*	56·0	51·0
102	1·580	33·6	*m*+	66·9	57·5
003	1·452	4·2	*w*−	11·8	12·4
110	1·325	11·1	*w*+	6·8	14·5
111	1·268	15·7	*m*	55·4	60·6
103	1·228	16·5	*m*	22·0	22·9
200	1·147	6·8	*w*−		
112	1·132	13·7	*w*+	50·4 }	88·9
201	1·109	12·5	*w*+		
004	1·090	1·9	*vw*		
202	1·015	9·7	*w*	30·4	40·8
104	0·984	9·6	*w*	64·9 }	69·0
113	0·978	9·0	*w*		
203	0·900	10·7	*w*+	13·2	11·4
005	0·872	1·7	*vw*		
210	0·867	10·7	*w*+	60·0 }	76·7
211	0·850	25·0	*m*		
114	0·842	13·5	*w*+		
105	0·815	16·1	*m*		
212	0·806	33·1	*m*+	76·7 }	64·9
204	0·790	22·2	*m*		

v = very; *s* = strong; *m* = medium; *w* = weak
$b_{Rh} = 0{\cdot}591 \times 10^{-12}$ cm
$b_{Li} = -0{\cdot}21 \times 10^{-12}$ cm

$a_0 = 2{\cdot}649 \pm 0{\cdot}003$ Å, $c_0 = 4{\cdot}359 \pm 0{\cdot}002$ Å, $C = 1{\cdot}646$. Calc. cell volume = 26·489 Å^3 with 2 atoms per cell and Calculated density* = 6·88 g.cm^{-3}.

The interatomic distances are:

Rh–Rh = 2·649 Å
Li–Li = 2·649 Å
Rh–Li = 2·663 Å

The space group is:

$P\bar{6}$ with
1 Rh (*a*) at: 0 0 0 and 1 Li (*d*) at: $\frac{1}{3}$ $\frac{2}{3}$ $\frac{1}{2}$

for which the structure factors take the following forms:

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† An abstract of this paper was presented at the Twenty-First Annual Pittsburgh Diffraction Conference, November 6–8, 1963, Mellon Institute, Pittsburgh, Pennsylvania.

* C. B. Magee. Average measured density of LiRh, 6·72 g.cm^{-3} (private communication). We are also indebted to Dr Magee for suggesting this investigation, and lending us a sample of LiRh prepared with normal lithium.

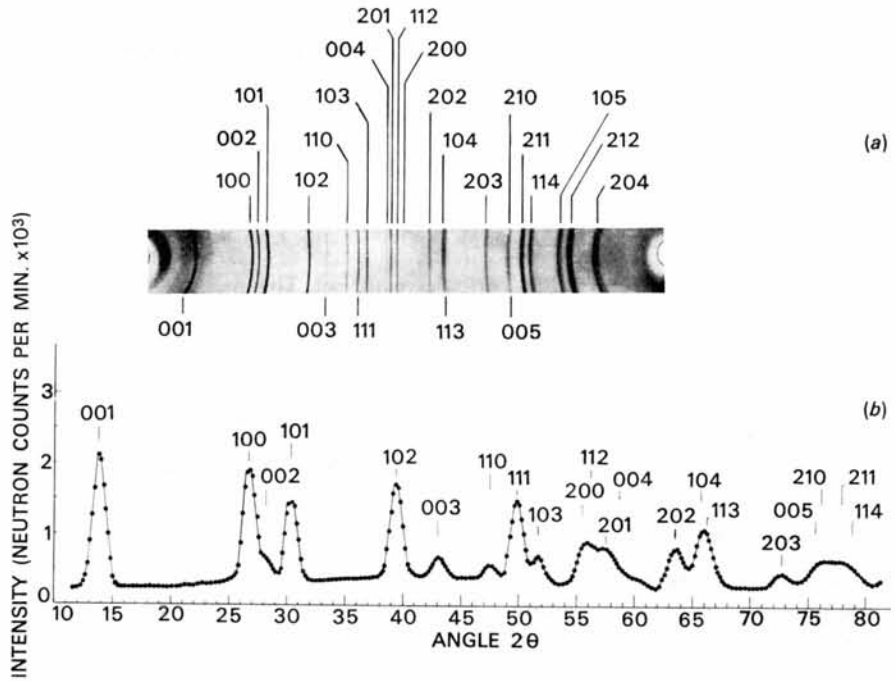

Fig. 1. Diffraction patterns of LiRh alloy. (*a*) Filtered Cu radiation (*b*) Neutron $\lambda = 1{\cdot}07$ Å.

(1) $|F| = f_{Rh} - f_{Li}$ for l odd, and $h+2k = 3n$,
(2) $|F| = f_{Rh} + f_{Li}$ for l even, and $h+2k = 3n$,
(3) $|F\bar{F}| = (f^2_{Rh} + f_{Rh}f_{Li} + f^2_{Li})$ for l odd and $h+2k = 3n \pm 1$,
(4) $|F\bar{F}| = (f^2_{Rh} - f_{Rh}f_{Li} + f^2_{Li})$ for l even and $h+2k = 3n \pm 1$,

where $n = 0, 1, 2, 3 \ldots$

The relative intensities for cylindrical samples were calculated from the following equations:

For X-rays,

$$I \propto |F|^2 m(1+\cos^2 2\theta)/\sin^2\theta \cos\theta \qquad (1)$$

For neutrons,

$$I \propto |F|^2 m(1/\sin^2\theta \cos\theta) A(\theta) (\exp[-2B \sin^2\theta/\lambda^2]) \qquad (2)$$

where m, $\frac{1}{2}(1+\cos^2 2\theta)$, $1 \sin^2\theta \cos\theta$, $A(\theta)$ and $\exp[-2B \sin^2\theta/\lambda^2]$ are the multiplicity, polarization, Lorentz, absorption and Debye–Waller factor, respectively.

Discussion

Rhodium and lithium atoms occupy preferred positions in the unit cell forming a layer structure with rhodium atoms in one layer and lithium atoms in the other, the layers alternating along c at $c_0/2$ distances apart. The nearest distance of approach between like atoms is the same but the unlike atoms are farther apart. The most interesting feature of the structure is the presence of 001, 003, 111, 113 and 005 reflections in both the X-ray and the neutron diffraction patterns. These reflections could result only from the occupation of preferred positions by each type of atom in the cell. The intensities calculated by assuming random occupation of the lattice sites by the atoms showed no agreement with the observed intensities.

While the agreement between the calculated and the observed intensities for the X-ray diffraction pattern was satisfactory, discrepancies in the intensities for neutron pattern were observed. Several sources for these discrepancies were considered; for example (1) a redetermination of the coherent nuclear scattering amplitude* of rhodium was made and was found to be $b_{Rh} = 0{\cdot}591 \times 10^{-12} \pm 0{\cdot}004$ cm; (2) the intensities were calculated by assuming vacancies in the lattice sites of rhodium and lithium atoms, but no significant improvement in the agreement was obtained, and (3) while there was no obvious indication of the presence of any impurity in the X-ray diffraction pattern, a contamination from compounds of lithium with light atoms such as Li_2O could not be overruled. This, however, did not affect the determination of the crystal structure reported here.

Thanks are due to Melvin H. Mueller, LeRoy Heaton and Richard L. Hitterman for help in measuring the coherent nuclear scattering amplitude of rhodium and helpful discussions.

References

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* Coherent nuclear scattering amplitude of rhodium; $b_{Rh} = 0{\cdot}60 \times 10^{-12}$ cm (Bacon, 1962); $b_{Rh} = 0{\cdot}585 \times 10^{-12}$ cm (Shirane, Nathans & Chen, 1964).