CONTRIBUTION NO. 1617 FROM THE CENTRAL RESEARCH DEPARTMENT,
EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE 19898

Chemistry of Noble Metal Oxides. II. Crystal Structures of $PtCoO_2$, $PdCoO_2$, $CuFeO_2$, and $AgFeO_2$

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Received November 21, 1969

Refined crystal structure parameters for $PtCoO_2$, $PdCoO_2$, $CuFeO_2$ (delafossite), and $AgFeO_2$ help to explain the high electrical conductivity of $PtCoO_2$ and $PdCoO_2$ and support the assignment of valence states for each compound. The coordination polyhedron for Pt and Pd is a hexagonal bipyramid with oxygen atoms at the apices and either Pt or Pd in the equatorial positions. The conductivity and short Pt–Pt (Pd–Pd) distances indicate strong metal–metal interactions. The relatively longer Cu–Cu and Ag–Ag distances are consistent with the semiconducting behavior of $CuFeO_2$ and $AgFeO_2$. The refinement results show that atom parameters for other similar phases such as $PdRhO_2$ can be reliably determined using only the Shannon and Prewitt effective ionic radii and the unit cells of these phases.

Introduction

The structure of delafossite, $CuFeO_2$, was confirmed by Pabst[1] to be the same as the structure of synthetic $CuFeO_2$ determined by Soller and Thompson.[2] Although some differences in structural parameters will be noted in the present work, the structure of $CuFeO_2$ is essentially correct. However, a certain amount of confusion about delafossite has been introduced into the literature. For example, Wyckoff[3] grouped the delafossite structure with the $CsCl_2I$ and the $NaFeO_2$ type structures. Although the rhombohedral space groups of these three structures are the same, the structures themselves are different and should not be indiscriminately grouped together.

Doubt about the existence of $CuFeO_2$ was raised by Buist, Gadalla, and White,[4] who were unable to synthesize $CuFeO_2$ and reported that this composition did not exist. This idea was refuted by Wiedersich, Savage, Muir, and Swarthout,[5] who used X-ray, Mössbauer, and chemical analysis techniques to verify the existence of $CuFeO_2$. The work of Wiedersich, *et al.*, has been further substantiated in part I of the present series of papers.[6]

In addition to the work of Soller and Thompson,[2] Pabst,[1] and Muir, *et al.*,[7] on the structure of $CuFeO_2$, a neutron diffraction investigation[8] confirmed the structure but did not significantly improve the crystallographic parameters. However, the Mössbauer and neutron diffraction work has established that the structure contains Cu^+ and Fe^{3+} rather than Cu^{2+} and Fe^{2+}. Although a number of other ABO_2 compositions with the same structure are known where A is Cu, Ag, or H and B is Al, Co, Cr, Fe, Ga, or Rh, almost all the structural results reported are the result of an assumed oxygen z parameter close to $^1/_9$. The only modern least-squares determinations of oxides with the delafossite structure are those of Hamilton and Ibers[9] for $HCrO_2$ and those of Delaplane, Ibers, Ferraro, and Rush for $HCoO_2$.[10] In addition, many of the cell parameters reported in the literature are inaccurate so that calculated interatomic distances are unreliable.

In part I[6] we reported the synthesis of several new phases having the delafossite structure which contain Pd or Pt in the A position. In this paper we report the results of crystal structure refinements used to investigate the composition and valence state of $PtCoO_2$ and $PdCoO_2$ and to provide reliable interatomic distances for $CuFeO_2$ and $AgFeO_2$. This information together with data from the Shannon and Prewitt[11] table of effective ionic radii and the cell parameters in part I enable us to predict the oxygen parameters very closely for any of the compositions given in part I.

Experimental Section

Crystals of $PtCoO_2$ and $CuFeO_2$ used for data collection were prepared hydrothermally as described in part I. Crystals of $PdCoO_2$ were produced by the metathetical reaction $PdCl_2 + 2CoO \rightarrow PdCoO_2 + CoCl_2$, also described in part I. The $AgFeO_2$ crystals were prepared hydrothermally by Croft, *et al.*[12]

Unit cell dimensions for $PtCoO_2$, $PdCoO_2$, $AgFeO_2$, and $CuFeO_2$ taken from part I[6] are reproduced in Table I. The space group of these compounds has been thought to be $R\bar{3}m$-D_{3d}^5 and we have seen no evidence to the contrary, either through examination of X-ray precession photographs taken of each type of crystal or in the least-squares structure refinements. Systematic absences in the diffraction data occur only when $-h + k + l = 3n$. There are three formula weights per hexagonal cell.

Structure Factor Data

Since single crystals of these compositions generally are found as thin hexagonal or triangular platelets, crystals were selected and mounted to take advantage of this morphology in order to minimize the transmission factors for the diffraction data used in the least-squares refinements. The crystals referred to in Table I were

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[1] A. Pabst, *Amer. Mineral.*, **31**, 539 (1946).

[2] W. Soller and A. J. Thompson, *Phys. Rev.*, **47**, 644 (1935).

[3] R. W. G. Wyckoff, "Crystal Structures," Vol. 2, 2nd ed, Wiley, New York, N. Y., 1964.

[4] D. S. Buist, A. M. M. Gadalla, and J. White, *Mineral. Mag.*, **35**, 731 (1966).

[5] H. Wiedersich, J. W. Savage, A. H. Muir, Jr., and D. G. Swarthout, *ibid.*, **36**, 643 (1968).

[6] R. D. Shannon, D. B. Rogers, and C. T. Prewitt, *Inorg. Chem.*, **10**, 713 (1971).

[7] A. H. Muir and H. Weidersich, *J. Phys. Chem. Solids*, **28**, 65 (1967).

[8] A. Apostolov, *God. Sofii Univ., Fiz. Fak.*, **59**, 47 (1966).

[9] W. C. Hamilton and J. A. Ibers, *Acta Crystallogr.*, **16**, 1209 (1963).

[10] R. G. Delaplane, J. A. Ibers, J. R. Ferraro, and J. J. Rush, *J. Chem. Phys.*, **50**, 1920 (1969).

[11] R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969).

[12] W. J. Croft, N. C. Tombs, and R. E. England, *ibid.*, **17**, 313 (1964).

TABLE I

CELL DATA FOR ABO_2 DELAFOSSITE STRUCTURES[a]

Crystal	a, Å	c, Å	V, Å^3	μ (Ag Kα), cm^{-1}	Crystal shape	Dimensions (max × min), mm	Transmission factors
$PtCoO_2$	2.8300 ± 4	17.837 ± 2	123.80	536	Equilateral triangular plate	0.10 × 0.009	0.08–0.61
$PdCoO_2$	2.8300 ± 2	17.743 ± 2	123.04	106	Hexagonal plate	0.15 × 0.018	0.31–0.90
$CuFeO_2$	3.0351 ± 1	17.166 ± 2	136.94	102	Hexagonal plate	0.26 × 0.0056	0.58–0.94
$AgFeO_2$	3.0391 ± 2	18.590 ± 2	148.69	86	Rectangular plate	0.10 × 0.034 × 0.022	0.44–0.82

[a] Space group $R\bar{3}m$. The c axes are always perpendicular to the crystal plates.

mounted so that the ϕ axis on the Picker diffractometer was normal to the c axis and parallel to a or a^* of each crystal. Then the transmission factors were large except for *hkl* with very small l. Reflections were recorded using Pd-filtered radiation from an Ag target X-ray tube, a scintillation detector with PHA, and a 2θ scan range of 2° plus the Kα_1–Kα_2 dispersion.

All crystals were single except for the $PtCoO_2$ platelet crystals which were always twinned by a 60° rotation around c. An attempt was made to grind spheres of untwinned, hydrothermally grown $PtCoO_2$ crystals, but only irregular egg-shaped crystals were obtained. The small transmission factors and small volumes of these crystals resulted in very unreliable diffraction data so we decided to use the twinned flakes for intensity measurements.

Absorption corrections were made using the method of Wuensch and Prewitt.[13] Even with very thin crystals, the absorption corrections are only approximate since even a small error in measurement of the crystal thickness can make a significant difference in the transmission factor. The dimensions of each crystal are given in Table I. For the absorption correction, each hexagonal plate was approximated as a disk. Corrections for the triangular and rectangular plates of $PdCoO_2$ and $AgFeO_2$ were calculated directly from the dimensions given in Table I.

Refinement

Structures were refined using a full-matrix, least-squares program and weighting scheme previously described by Prewitt and Sleight.[14] Reflections for which the transmission factor was very small were eliminated from the refinement. The refinements were routine except for $PtCoO_2$ where the data came from a twinned crystal. Here it was possible to select two unique sets of reflections from each individual (or similarly oriented individuals) plus a set containing contributions from both individuals. These were then combined into one set by using scale factors obtained from each individual set. (See Table II for structure factors.) However, the error calculated for the oxygen position in $PtCoO_2$ is very large and this is reflected in the interatomic distances discussed below. Table III gives the refined parameters and R's $[R = \Sigma||F_o| - |F_c||/\Sigma|F_o|; wR = ((\Sigma w||F_o| - |F_c||)^2/(\Sigma w|F_o|)^2)^{1/2}]$ for each of the structures.

TABLE II

STRUCTURE FACTORS FOR $PtCoO_2$, $PdCoO_2$, $CuFeO_2$, AND $AgFeO_2$[e]

			$PtCoO_2$[a]		$PdCoO_2$[b]	
h	k	l	Fobs	Fcal	Fobs	Fcal
3	0	0	120	111*	201	194
1	1	0	137	171*	305	295
2	2	0	103	102*	173	170
1	3	1	60	59	54	57
3	2	1	45	48	43	47
0	2	1	86	86	89	87
2	1	1	71	74	71	71
4	0	1	51	53	55	52
1	0	1	106	106	151	137
2	0	2	129	135	239	245
3	1	2	88	91	149	149
0	1	2	165	156	329	324
1	2	2	115	116	201	195
2	3	2	74	76	121	124
0	4	2	81	83	134	135
0	3	3	63	59	36	38
2	2	3	71	53*	33	36
1	1	3	88	75*	44	43
0	0	3	123	88*	68	54
1	0	4	134	146	237	271
4	0	4	72	77	124	118
2	1	4	102	108*	171	166
0	2	4	122	123	205	200
1	3	4	101	84	128	129
0	4	5	42	45	21	25
1	2	5	57	60*	29	28
0	1	5	69	73*	25	22
3	1	5	47	49	21	27
2	0	5	62	66	28	26
0	0	6	193	183*	288	328
1	1	6	149	142*	231	225
2	2	6	105	91*	141	140
0	3	6	109	100	161	157
1	3	7	54	54	44	46
0	2	7	78	77	67	62
2	1	7	66	68*	56	54
4	0	7	47	49	41	42
1	0	7	88	93*	90	83
2	0	8	129	135*	227	242
3	1	8	88	91	154	153
0	1	8	154	168*	308	313
1	2	8	109	117*	199	197
0	4	8	82	83	139	139
0	3	9	71	65	68	66
2	2	9	68	59*	59	60
1	1	9	102	88*	96	91
0	0	9	133	114*	140	137
1	0	10	144	159*	266	303
4	0	10	76	80	135	137
2	1	10	107	112*	191	190
0	2	10	124	128*	230	226
1	3	10	85	89*	151	150
0	4	11	48	46	37	40
1	2	11	66	62*	51	52
0	1	11	81	81	73	69
3	1	11	53	51	39	44
2	0	11	69	70	57	57
0	0	12	163	149*	235	252
1	1	12	135	123*	195	193
2	2	12	96	84*	129	130
0	3	12	99	91*	145	145

			$CuFeO_2$[c]		$AgFeO_2$[d]	
h	k	l	Fobs	Fcal	Fobs	Fcal
3	0	0	175	179	122	119
4	1	0	97	99	68	66
1	-1	0	311	307	210	201
2	2	0	150	148	103	99
1	4	0	97	99	65	66
1	3	1	0	17*	30	31
3	2	1	0	9*	21	22
0	2	1	47	52	61	61
2	1	1	26	34	45	46
4	0	1	0	12*	21	26
1	0	1	102	93	105	100
2	0	2	235	237	160	160
3	1	2	121	121	87	85
0	1	2	354	330	230	227
1	2	2	185	180	124	123
2	3	2	91	91	63	64
0	4	2	106	104	71	74
1	4	3	23	16	4	9
0	3	3	19	10	17	21
2	2	3	22	12	14	18
1	1	3	16	8	34	32
4	1	3	23	16	17	9
0	0	3	27	25	47	45
1	0	4	240	242	175	179
4	0	4	78	79	62	62
2	1	4	142	139	106	102
0	2	4	191	180	128	130
3	2	4	71	69	53	55
1	3	4	96	93	71	72
0	4	5	34	26	7	9
2	3	5	31	26	8	7
1	2	5	36	27	17	16
0	1	5	61	53	21	21
3	1	5	33	25	10	12
2	0	5	37	32	22	19
0	0	6	262	294	222	216
4	1	6	67	67	53	53
1	1	6	213	202	157	148
2	2	6	103	103	81	79
0	3	6	129	124	95	94
1	4	6	67	67	51	53
1	3	7	9	3	23	23
3	2	7	14	7	17	16
0	2	7	10	10	42	42
2	1	7	0	4*	35	33
4	0	7	15	6	15	19
1	0	7	25	20	66	61
2	0	8	224	222	157	155
3	1	8	123	121	90	86
0	1	8	300	304	212	214
1	2	8	179	174	124	122
2	3	8	94	94	68	66
0	4	8	109	106	72	75
0	3	9	23	26	37	38
2	2	9	15	20	31	32
1	1	9	57	54	65	62
0	0	9	101	91	103	98
1	0	10	271	289	192	198
4	0	10	107	108	74	73
2	1	10	176	172	121	116
0	2	10	224	216	143	145
3	2	10	96	96	65	64
1	3	10	125	123	85	83
0	4	11	6	2	12	17
2	3	11	5	0	12	14
1	2	11	13	14	32	30
0	1	11	44	36	51	50
3	1	11	8	5	18	21
2	0	11	25	22	41	37
0	0	12	230	238	164	163
1	1	12	187	175	128	122
2	2	12	102	98	75	71
0	3	12	122	115	85	83

[a] s = 0.76. [b] s = 2.07. [c] s = 2.68. [d] s = 1.41. [e] In each set the structure factors should be divided by the indicated scale factor, s, to give an absolute scale. Asterisks indicate reflections omitted from the final cycles of refinement because of absorption or twinning problems.

Discussion

Figure 1 is a diagram representing the delafossite-type structure with the actual dimensions taken from the $PtCoO_2$ refinement. As can be seen in Figure 1, the

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(13) B. J. Wuensch and C. T. Prewitt, *Z. Kristallogr., Kristallogeometrie, Kristallphys., Kristallchem.*, **122**, 24 (1965).

(14) C. T. Prewitt and A. W. Sleight, *Inorg. Chem.*, **7**, 1090 (1968).

TABLE III

RESULTS OF LEAST-SQUARES REFINEMENT[a]

	$PtCoO_2$	$PdCoO_2$	$CuFeO_2$	$AgFeO_2$
C	$4.1\ (1.5) \times 10^{-6}$	$2.6\ (1.3) \times 10^{-7}$	$2.4\ (0.9) \times 10^{-7}$	$4.1\ (1.3) \times 10^{-7}$
B(A ion)	0.19 (7)	0.16 (4)	0.93 (4)	0.78 (3)
B(B ion)	0.15 (11)	0.15 (4)	0.34 (4)	0.46 (3)
z(oxygen)	0.1140 (62)	0.1112 (8)	0.1066 (5)	0.1112 (5)
B(oxygen)	0.64 (48)	0.34 (15)	0.25 (0.09)	0.66 (9)
R	0.046	0.041	0.051	0.035
wR	0.057	0.058	0.074	0.037

[a] Standard errors are given in parentheses. C is the secondary extinction parameter.[14] Coordinates for the A ion are 0, 0, 0, and for the B ion 0, 0, 1/2, and for oxygen 0, 0, z. The R quoted for $PtCoO_2$ is for the reflections included in the least-squares refinement; R for all reflections is 0.072. Units for the isotropic temperature factors (B's) are Å^2.

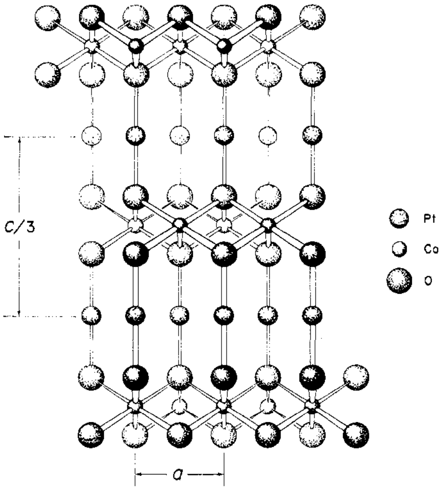

Figure 1.—$PtCoO_2$ (delafossite) structure.

TABLE IV

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (DEG) FOR ABO_2 DELAFOSSITE STRUCTURES

	$PtCoO_2$	$PdCoO_2$	$CuFeO_2$	$AgFeO_2$
		Distances		
A–A[a]	2.830	2.830	3.035	3.039
B–B[a]	2.830	2.830	3.035	3.039
A–B[a]	3.392	3.379	3.355	3.588
A–O	2.03 (11)	1.973 (13)	1.835 (8)	2.067 (8)
B–O	1.89 (5)	1.908 (7)	2.033 (4)	2.035 (4)
O^+–O^+ [a]	2.830	2.830	3.035	3.039
O^+–O^-	2.49 (8)	2.558 (10)	2.706 (6)	2.707 (6)
		Angles		
A–O–B	119.9	121.1	120.2	122.0
B–O–B	97.3	95.7	96.6	96.6
O^+–B–O^+	97.3	95.7	96.6	96.6
O^+–B–O^-	82.7	84.2	83.4	83.4

[a] Standard errors for these distances are fixed by the cell parameters.

platinum and cobalt atoms occupy alternate layers in the structure which are normal to c. The platinum atoms are linearly coordinated by two oxygen atoms whereas the cobalt atoms are octahedrally coordinated by oxygen atoms. If the surrounding platinum atoms are also considered as part of the coordination polyhedron, Pt is in a hexagonal bipyramid with oxygen atoms at the apices and platinum atoms at the six equatorial positions. This latter coordination has not been explicitly discussed in previous work on delafossite-type structures, but good evidence is given below and in part III that there is Pt–Pt interaction in this structure. Hexagonal bipyramidal coordination is rarely found so this in itself is an important aspect of the $PtCoO_2$ structure.

Table IV lists the interatomic distances and bond angles for each of the structures examined. Probably the most important information to be gained from these data is support for the formal valence to be assigned to each ion in the structure. Although Pabst pointed out that two-coordinated Cu in $CuFeO_2$ strongly suggests the presence of Cu^+ rather than Cu^{2+}, the interatomic distances in Table IV further substantiate the presence of monovalent Cu, Ag, Pt, and Pd in these delafossite-type structures. Part I discussed the evidence which established that Cu^+ and Fe^{3+} are present in $CuFeO_2$ and this can be substantiated by comparing the Fe–O distance of 2.03 Å calculated from effective ionic radii for six-coordinated Fe^{3+} and four-coordinated oxygen ($O(IV)^{2-}$) to the value of 2.033 Å in Table IV for $CuFeO_2$ and 2.035 Å for $AgFeO_2$. Using the above radius for $O(IV)^{2-}$, radii for $Cu(II)^+$ and $Ag(II)^+$ of 0.46 and 0.69 Å are also determined. Using the same approach, the Co–O distances of 1.89 ± 5 and 1.908 ± 7 Å in $PtCoO_2$ and $PdCoO_2$ are consistent with 1.905 Å calculated for $Co(VI)^{3+}$LS–$O(IV)^{2-}$. Then, if the crystals are stoichiometric, Pt and Pd must be formally monovalent. This deduction must be examined carefully because such valence states have not been reported previously. Although this premise is discussed in detail in part III, it seems appropriate to point out several structural considerations here.

As noted in parts I and III, the electrical conductivities of both $PdCoO_2$ and $PtCoO_2$ are very anisotropic and highest when measured in the plane containing the a axis. This suggests metal–metal interaction which is supported by the Pd–Pd and Pt–Pt distances of 2.83 and 2.83 Å which are close to those found in the fcc metals (Pd–Pd, 2.75 Å; Pt–Pt, 2.77 Å). In contrast, the Cu–Cu and Ag–Ag distances of 3.035 and 3.039 Å in $CuFeO_2$ and $AgFeO_2$ are considerably longer than in the metals (Cu–Cu, 2.56 Å; Ag–Ag, 2.89 Å). This is consistent because $CuFeO_2$ and $AgFeO_2$ exhibit semiconducting rather than metallic behavior.

Because of uncertainty about whether the composition $Pt^+Co^{3+}O_2$ or $Pt^{2+}{}_{0.8}Co^{3+}{}_{0.8}O_2$ is correct, both models were tried in the least-squares refinements, but the results were inconclusive. Both refinements re-

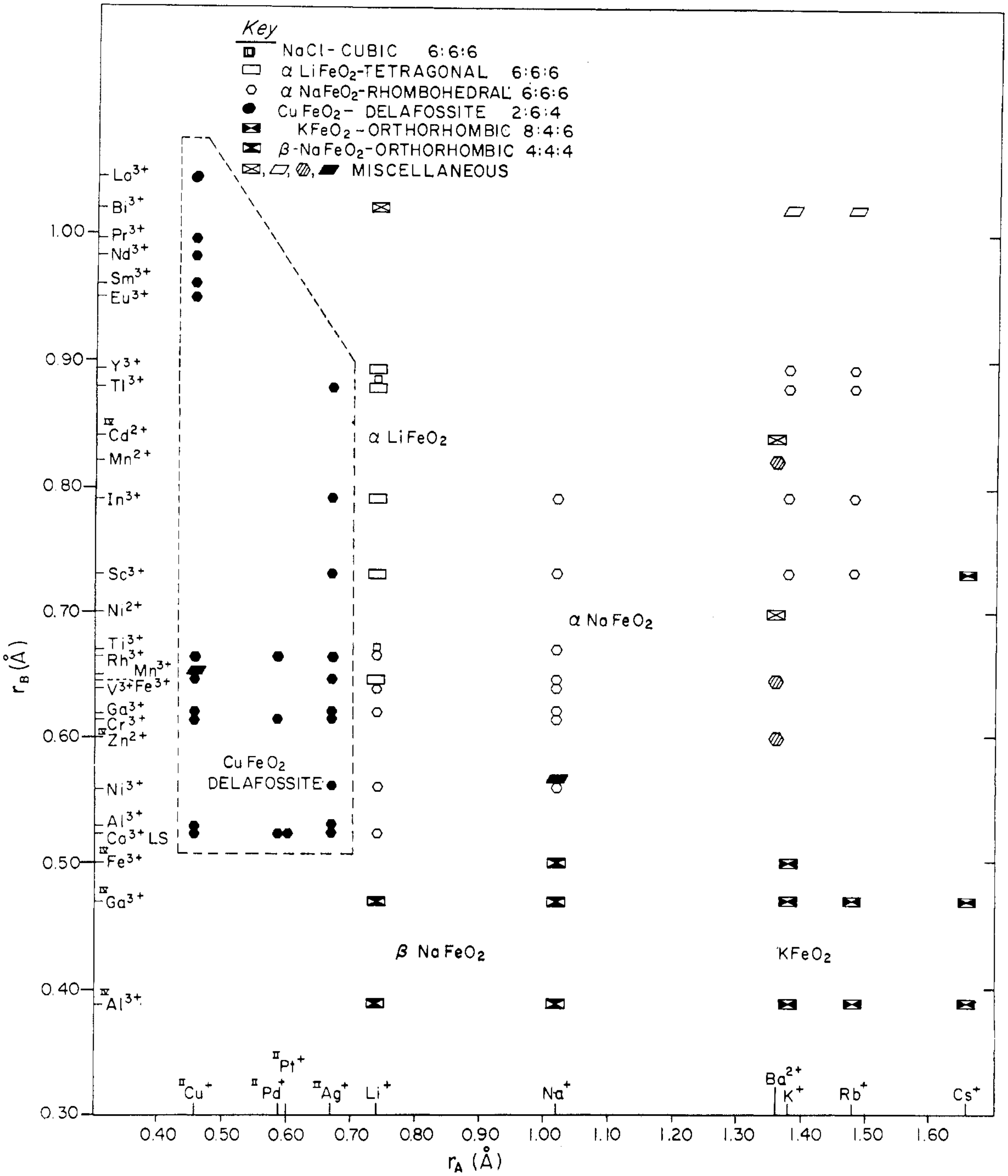

Figure 2.—Plot of r_A *vs.* r_B for various ABO_2 phases.

sulted in *R*'s of 0.04 and the only observed differences were in the refined temperature factors. The trouble here seems to be that the problems of data measurements plus the domination of the intensities by the heavy metals prevent a reliable determination of the metal:oxygen ratio. There is evidence that when cation sites are shared between two sizes of cations the interatomic distances observed in diffraction experiments are intermediate between those expected for each of the two cations. Similarly, one would expect the Co–O distance to be smaller than usual if the site contained 20% oxygen vacancies. Since this is not the case, the only conclusion that can be drawn from the X-ray measurements is that $PtCoO_2$ is nearly stoichiometric.

Although the isotropic temperature factors given in Table III show a large variation, it is probably not wise to provide much physical interpretation of these numbers. The difficulty of making accurate absorption corrections certainly influences the temperature factors as does the secondary extinction correction.

The effective ionic radii of Shannon and Prewitt[11] can be used to estimate structure parameters for other ABO_2 delafossites without having to resort to diffraction intensity measurements. If we take, for example, the unit cells of $PdRhO_2$, $CuRhO_2$, and $AgRhO_2$ from

Table II of part I and the Rh(VI)$^{3+}$ radius of 0.665 Å, oxygen z parameters of 0.1076, 0.1072, and 0.1117 are found. This results in 1.95 Å for Pd–O, 1.83 Å for Cu–O, and 2.08 Å for Ag–O which compare well with the equivalent distances in Table IV.

Radii are also effective in comparing the delafossite structure types with those of other ABO_2 phases. Figure 2 shows a plot of r_A *vs.* r_B for the various known ABO_2's. With few exceptions, this plot gives a good idea of the structure to be expected for a particular composition. It also suggests new compositions which might be synthesized.

Acknowledgment.—The authors are grateful to Professor A. Pabst of the University of California for reviewing the manuscript. He also provided us with synthetic crystals of $AgFeO_2$ prepared by Dr. W. J. Croft and natural crystals of delafossite, $CuFeO_2$.

CONTRIBUTION NO. 1678 FROM THE CENTRAL RESEARCH DEPARTMENT,
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Chemistry of Noble Metal Oxides. III. Electrical Transport Properties and Crystal Chemistry of ABO_2 Compounds with the Delafossite Structure

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Received April 15, 1970

A schematic model of chemical bonding for the ternary oxides ABO_2 (where A is Cu, Ag, Pd, or Pt and B is a trivalent ion such as Cr^{3+}, Fe^{3+}, Co^{3+}, or Rh^{3+}) is described. This model is shown to rationalize several features of the crystal chemistry of these compositions, including their common adoption of the delafossite-type structure. Electrical conductivity measurements as functions of temperature and crystallographic orientation are described and the results are shown to be qualitatively explainable on the basis of the proposed bonding scheme. All of the subject oxides exhibit anisotropic electrical conductivity that is metallic when A is Pt or Pd but semiconducting when A is Cu or Ag.

Introduction

Recent applications of low-temperature or high-pressure synthesis techniques have led to the discovery of several new polynary oxides containing elements of the platinum and coinage groups. In part I of this series some aspects of the general chemistry of such oxides were considered, and synthesis of ternary compositions having the general formula ABO_2 (where A is Pd, Pt, Cu, or Ag and B is one of the other transition elements) were described. Structural refinements of several of these ABO_2 compounds, which are isotypic with the mineral delafossite ($CuFeO_2$), were reported in part II. As discussed in that paper, the A ions in delafossite have only two anion near neighbors, while the B ions occur in regular octahedral interstices. Each oxygen is coordinated by four cations, one A and three B, at the corners of a tetrahedron.

The platinum and palladium analogs ($PtCoO_2$, $PdCoO_2$, $PdCrO_2$, and $PdRhO_2$) were the first of the delafossite type to be investigated by us. In addition to being among the first well-characterized oxides in which Pt or Pd occurs in combination with other transition metals, the structure and properties of these compositions presented several other unusual features. (1) Twofold, linear coordination by anions had not previously been observed for platinum or palladium. (2) Magnetic susceptibility measurements and Co–O distances indicated that cobalt in $PtCoO_2$ and in $PdCoO_2$ was in a trivalent, low-spin state. This conclusion was supported by the fact that chromium and rhodium could be wholly substituted for cobalt in the palladium analog. Since a trivalent oxidation state is the most stable for both Cr and Rh, there was little doubt that palladium in these compounds was formally present in the highly unusual monovalent state. (Similar reasoning would indicate Pt^+ in $PtCoO_2$; however, as pointed out in part I, the possibility of nonstoichiometry in the platinum composition, giving $Pt^{2+}{}_{0.8}Co^{3+}{}_{0.8}O_2$, cannot be excluded.) (3) Preliminary electrical resistivity measurements showed that single-crystal, hexagonal plates of the platinum composition exhibited exceptionally high electrical conductivity (10^6 ohm^{-1} cm^{-1}) in the plane of the plate (*i.e.*, perpendicular to the crystallographic c axis). Such a high metal-like conductivity is, in itself, quite uncommon for oxides, but even more unusual was an apparently large anisotropy of this property. Consideration of these features of the platinum and palladium delafossite phases has led to the development of a qualitative model for the chemical bonding in these oxides that appears to rationalize their crystal chemistry and electrical behavior. General application of this model suggests that $PdCoO_2$, $PdCrO_2$, and $PdRhO_2$ should have electrical properties analogous to those of $PtCoO_2$, but that copper and silver analogs should be semiconducting. In order to check this point, we made a careful study