Tetragonal phases of the general type $10M_2O_5.90M'_2O_5$ apparently isostructural with $Ta_2O_5.2Nb_2O_5$.

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A study of the solid-state reactions in the V_2O_5–Nb_2O_5 system (Waring & Roth, 1963) has shown that the phase designated by Goldschmidt (1960) as $[\beta'(Nb,V)_2O_5]$ can be indexed on the basis of a body-centered tetragonal cell with $c = 3.821$, $a = 15.72$ Å.

An investigation was made to determine whether or not this phase occurred in other binary systems. Oxide mixtures were weighed, pressed into disks, and calcined at appropriate temperatures (ranging from 200 to 1000 °C) necessary to achieve physical homogeneity. Portions of these combined mixtures were reheated in sealed platinum tubes to temperatures sufficient to form this phase (Table 1). The phases were identified by X-ray diffraction at room temperature using a high-angle recording Geiger-counter diffractometer and Ni-filtered Cu K radiation.

Table 1. *Preparation and unit-cell dimensions of mixed oxides*

Composition (mol.%)	Unit-cell dimensions		Heat treatment	
	a (Å)	c (Å)	Temp. (°C)	Time (hr)
$10P_2O_5:90Nb_2O_5$	15·60	3·828	1284	69
$10As_2O_5:90Nb_2O_5$	15·63	3·816	950	19
$10GeO_2:90Nb_2O_5$	15·70	3·817	1323	19
$10V_2O_5:90Nb_2O_5$	15·72	3·821	1294	25
$33·33Ta_2O_5:66·67Nb_2O_5$	15·75	3·821	1475	16
$10P_2O_5:90Ta_2O_5$	15·52	3·823	1000	2
$10As_2O_5:90Ta_2O_5$	15·58	3·822	1000	9
$10V_2O_5:90Ta_2O_5$	15·66	3·820	1247	6

The data (Table 1) show that 10 mol.% P_2O_5, As_2O_5 or V_2O_5 when added to 90 mol.% of either Nb_2O_5 or Ta_2O_5 gives X-ray diffraction patterns which could be indexed on a tetragonal cell.

A similar tetragonal phase also forms when 10 mol.% GeO_2 are added to Nb_2O_5 but not in the GeO_2–Ta_2O_5 system.

The powder data of these tetragonal phases appear to indicate that they are isostructural with the $Ta_2O_5.2Nb_2O_5$ compound previously reported by Holtzberg & Reisman (1961) as being cubic. The powder diffraction pattern of $Ta_2O_5.2Nb_2O_5$ was indexed in this laboratory on the basis of a tetragonal cell, having $c = 3.821$, $a = 15.75$ Å. This cell was independently verified from single-crystal measurements by Mohanty, Fregel & Healy (1962).

All the X-ray powder diffraction patterns of the phases listed in Table 1 are similar to the $Ta_2O_5.2Nb_2O_5$ pattern, and data are given (Table 2) for $10P_2O_5:90Nb_2O_5$; it shows greatest distortion from a pseudo-cubic structure.

The following comments about the structure of these tetragonal phases can be made from the data available:

1. The fact that phases with 1:9 M:M′ ratios are apparently isostructural with a 1:2 M:M′ phase ($Ta_2O_5.2Nb_2O_5$) indicates that either the cation ordering

is different for the two different ratios or that the cations are disordered.

2. The fact that P^{5+} is accepted into this structure indicates that there is very likely at least one out of ten cation sites which is tetrahedrally coordinated, assuming cation ordering, or the unlikely possibility exists that the P^{5+} might be in octahedral coordination.

Table 2. *X-ray diffraction powder data for* $10P_2O_5.90Nb_2O_5$

(Cu $K\alpha_1$ radiation)

		$1/d^2$		
hkl	*d*	Obs.	Calc.*	I/I_0†
110	10·99 Å	0·0083 Å⁻²	0·0082 Å⁻²	3
200	7·79	0·0165	0·0164	5
220	5·51	0·0329	0·0329	3
310	4·93	0·0412	0·0411	23
400	3·90	0·0658	0·0658	5
101	3·72	0·0724	0·0724	52
420	3·486	0·0823	0·0822	100
211	3·352	0·0890	0·0888	23
510	3·056	0·1071	0·1069	23
321	2·865	0·1218	0·1217	58
411	2·690	0·1382	0·1381	15
530	2·673	0·1400	0·1398	5
620	2·466	0·1644	0·1644	14
501	2·417	0·1711	0·1710	9
521	2·309	0·1875	0·1875	9
710/550	2·205	0·2058	0·2055	2
640	2·162	0·2139	0·2138	4
611	2·130	0·2204	0·2203	9
541	2·055	0·2366	0·2368	4
730	2·049	0·2385	0·2384	25
800	1·950	0·2631	0·2631	4
002	1·914	0·2730	0·2730	14
820	1·892	0·2792	0·2795	2
202	1·858	0·2896	0·2894	2
750	1·812	0·3046	0·3042	8
312	1·784	0·3139	0·3141	5
651	1·770	0·3191	0·3190	3
840	1·744	0·3287	0·3289	7
811/741	1·727	0·3353	0·3354	19
422	1·678	0·3549	0·3552	17
831	1·648	0·3685	0·3683	7

* Based on tetragonal cell, $c = 3.828$, $a = 15.60$ Å.
† Relative intensity.

3. The fact that Ge^{4+} is accepted into this structure indicates that either the oxygen content may vary or minor differences exist in the packing of the cation coordination polyhedra.

The problems posed by these observations can only be resolved by single-crystal studies which are presently in progress. These studies should establish whether the tetragonal phases have the same structures or different structures which cannot be distinguished by the X-ray powder diffraction technique.

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Space group identification by proton magnetic resonance. By R. CHIDAMBARAM, *Atomic Energy Establishment, Trombay, Bombay, India*

The method of identifying the space group of a crystal by studying the systematic absences of certain classes of reflexions in the X-ray diffraction pattern is often ambiguous, owing mainly to the Friedel law, which introduces an artificial centre of symmetry into the pattern. The purpose of this note is to point out that it is often possible to resolve this ambiguity by examining the magnetic resonance pattern of the protons in the crystal.

The resonance pattern for a 2-proton system (like a water molecule) inside a crystal consists of a doublet, and by studying the doublet separation for a sufficiently large number of orientations with respect to the steady magnetic field both the length and the orientation inside the unit cell of the inter-proton vector (hereinafter called the *p–p* vector) can be determined (Pake, 1948). The complete resonance pattern for any crystal containing 2-proton systems will be a superposition of the doublets from the various non-parallel *p–p* vectors in the unit cell (the pattern would also contain the lines from the other protons in the unit cell but it is possible to isolate them).

Now, the procedure of using proton magnetic resonance data to identify space groups consists in first calculating the number of non-parallel *p–p* vectors in the unit cell and their mutual symmetry relationships for the two or more space group choices provided by the X-ray method, and then determining which of them fits the experimental pattern. We will now consider a few examples to show the application of the method:

(*a*) *P*1 and *P*$\bar{1}$. Two *p–p* vectors in the unit cell of a crystal of space group *P*1 would be mutually unrelated and non-parallel while in the space group *P*$\bar{1}$ they would be related by the centre of symmetry so that there would be only one non-parallel vector.

(*b*) *Cc* and *C*2/*c*. Four *p–p* vectors in the unit cell of a crystal of space group *Cc* may be placed in general positions and the resonance pattern will be that due to 2 non-parallel vectors related by mirror symmetry across the (010) plane, whereas in the space group *C*2/*c* these vectors have to be placed in special positions lying on twofold axes so that there would be only one non-parallel vector lying in the (010) plane.

The latter example applies to the case of potassium oxalate monohydrate, regarding whose space group there has been some dispute (Jeffrey & Parry, 1954). It was shown by Chidambaram (1961) that the *p–p* vectors of this crystal lie within ±1° of the (010) plane so that the space group is most likely to be *C*2/*c*. The structure of this crystal has been refined successfully on the basis of this space group both by X-ray diffraction (Ramaseshan, Vaidya & Swaminathan, 1964) and by

neutron diffraction (Chidambaram, Sequeira & Sikka, 1964). Recently, Pedersen & Holcomb (1963) have also examined the proton magnetic resonance of this crystal and assigned it to the space group *C*2/*c*.

The following points may be noted:

1. Though in principle the method is applicable to resonance patterns obtained from protons in spin systems more complicated than 2-proton systems, unscrambling the experimental curves is difficult and often impossible in these cases. This limits the application of the method to crystals containing H_2O molecules or CH_2 groups. It could probably be extended to crystals containing NH_2 groups if one used double nuclear resonance and washed out the dipolar interaction due to the N nucleus. Between them, however, these groups cover quite a large number of crystals.

2. *Ab initio* it is not possible to proceed from the proton magnetic resonance data. For example, four *p–p* vectors in a unit cell of a crystal of space group *P*2/*m*, *P*2/*c*, *P*2₁/*m*. *P*2₁/*c*, *Cm*, *C*2 or *Cc* would give the same pattern symmetry. The method has, therefore, to be applied at the stage when the X-ray diffraction data have given the number of formula units in the unit cell and the systematic absences have afforded the space group alternatives. Sometimes the choice may also not be complete. For example, *P*2/*m* can be distinguished from *Pm* and *P*2 but the latter are usually indistinguishable from each other.

3. There is a small but finite probability that the configuration of the *p–p* vectors may simulate a symmetry (within the accuracy of the experiment) which is higher than what is required by the space group. Such difficulties due to pseudo-symmetry are also sometimes encountered in the statistical methods of analysing X-ray intensities to distinguish a centre of symmetry.

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