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Preparation and Structure of the Compounds $SrVO_3$ and Sr_2VO_4

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The compounds $SrVO_3$ and Sr_2VO_4 have been synthesized by decomposition of the nitrates in air followed by high purity hydrogen reduction. $SrVO_3$ crystallizes in a cubic perovskite structure with a = 3.841 Å. This result shows the incorrectness of its A.S.T.M. card. The structure of Sr_2VO_4 has been studied by X-ray and neutron diffraction measurements. Sr_2VO_4 presents a tetragonal K_2NiF_4-type structure with $a = b$ = 3.837 Å and c = 12.576 Å.

Introduction

Since the discovery of superconductivity below 30 K in the La–Ba–Cu–O system (*1*), there has been extensive research work on new compounds based on the perovskite structure for better understanding of the mechanism for the high-T_c superconductivity. We have been interested in compounds where the cation Cu d^9 in high-T_c superconductors would be replaced by a d^1 cation, for example, the ion V^{4+}. This present work deals with the synthesis and the cristallographic study of the two compounds $SrVO_3$ and Sr_2VO_4.

Experimental

A slurry formed by a suspension of vanadium oxide V_2O_5 in a strontium nitrate $Sr(NO_3)_2$ solution (in proportions Sr/V = 1 for $SrVO_3$ and Sr/V = 2 for Sr_2VO_4) is transformed into powder by spray-drying. The obtained mixture is calcined in air in order to decompose the nitrates (700°C—7 hr for $SrVO_3$ and 800°C—5 hr for Sr_2VO_4). Finally, the V^{5+} ion is reduced to V^{4+} by a treatment in pure hydrogen in a metallic furnace: For $SrVO_3$, the calcined powder is pressed into 8-mm-diameter pellets at 200 MPa and treated at 1000°C for 24 hr. For

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Sr_2VO_4, the pellets pressed at 200 MPa and transformed into 250-μm-diameter granules are treated at 1000°C for 48 hr.

The resulting materials, after each treatment, were characterized by X-ray diffraction with a Siemens goniometer using Co*Kα* radiations. The structural study of Sr_2VO_4 was completed by neutron diffraction at the Institute Laue-Langevin (Grenoble). Thermogravimetric analyses were carried out with a Setaram TB 85 16-18 thermobalance.

Results and Discussion

1. Study of SrVO$_3$

After the intermediate calcination in air at 700°C, X-ray diffraction analysis shows the presence of the phases $Sr_2V_2O_7$ and $Sr_3V_2O_8$. The Sr/V ratio (= 1) suggests the presence of unreacted vanadium oxide not detectable by the X-ray analysis. The reduction under hydrogen atmosphere of the calcinated mixture was first followed by thermogravimetric analysis (1000°C—1 hr). The weight loss observed, 4.7% for 4.1% in theory, means that the V^{5+} ion has been reduced to V^{4+} (cf. Fig. 1). The powder, originally white, turned black.

After the reduction (1000°C—24 hr), a single phase was formed and presents a cubic perovskite-like structure iostopic with the so-called compound $SrVO_{2.5}$ (*2*) (cf. Fig. 2) (cf. A.S.T.M. Card 11-25). The phase can be written as $SrVO_{3-x}$, where x represents the amount of oxygen vacancies. In order to determine the oxygen deficiency in the compound, a controlled oxidation in He–1000 ppm O_2 has been undertaken by thermogravimetric analysis (cf. Fig. 3). This experiment shows that the filling of vacancies occurs before the oxidation of the compound $SrVO_3$ into $Sr_2V_2O_7$.

From the thermogravimetric data, we can, on the one hand, determine the value of x if we suppose that the compound is $SrVO_{3.00}$ at the point of inflection of the curve and, on the other hand, control the formation of stoichiometric $SrVO_{3.00}$.

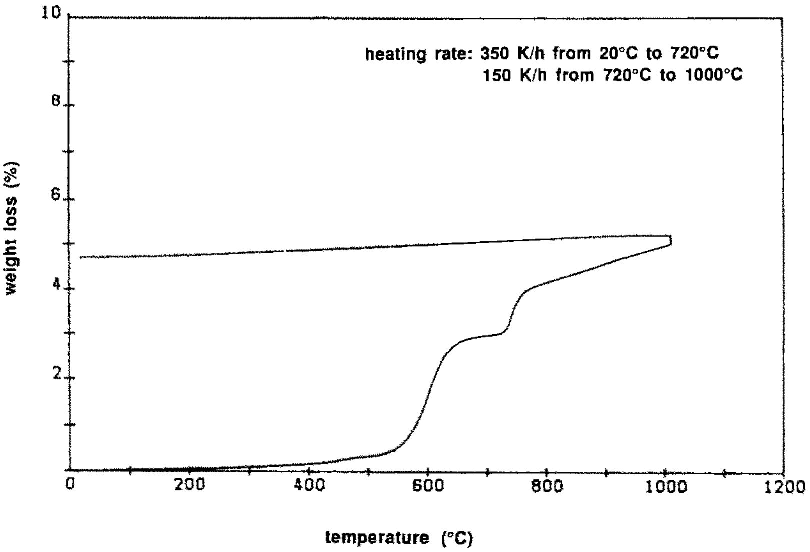

FIG. 1. Sr/V = 1: thermogravimetric curve of the reduction under H_2 atmosphere (1000°C—1 hr).

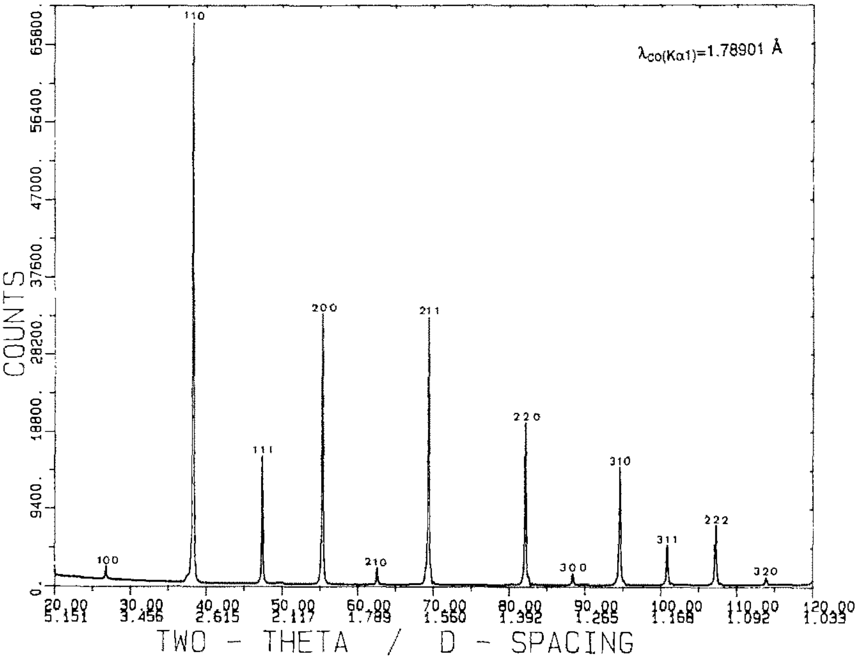

FIG. 2. Sr/V = 1: X-ray diffraction pattern of the H_2-annealed sample (1000°C—24 hr).

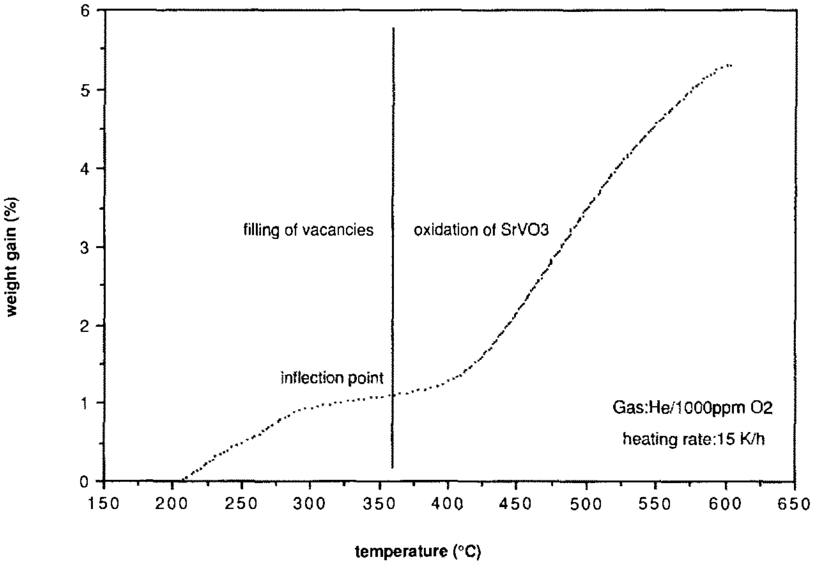

FIG. 3. Sr/V = 1: thermogravimetric curve of the controlled oxidation of $SrVO_{3-x}$.

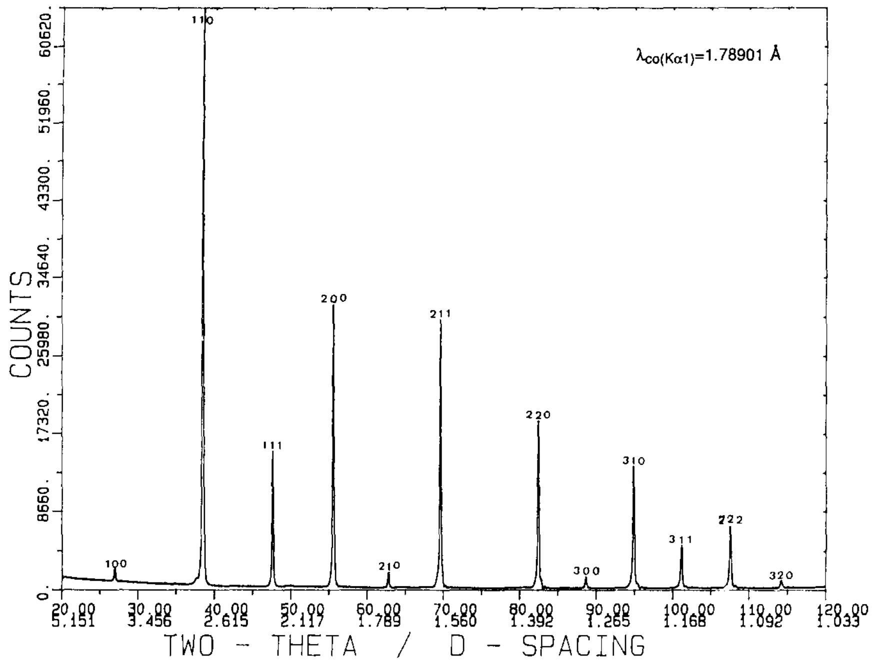

FIG. 4. X-ray diffraction pattern of $SrVO_{3.00}$.

After two agreeing experiments, we can say that the H_2-annealed sample is $SrVO_{2.88(\pm 0.01)}$.

X-ray diffraction patterns of $SrVO_{2.88}$ (cf. Fig. 2) and $SrVO_{3.00}$ (cf. Fig. 4) are characteristic of a cubic perovskite structure, with $a = 3.846(6)$ Å and 3.840(9) Å, respectively. A list of interplanar spacings, *h k l* indices, and relative intensities is presented in Tables I and II.

These results show that the compound $SrVO_{3.00}$ crystallizes in a cubic and not orthorhombic perovskite structure as reported by Palanisamy *et al.* (*3*) (cf. A.S.T.M. Card 32-1267). We identified the orthorhombic structure, proposed by him, as a mixture of $SrVO_3$ and a small amount of orthovanadate $Sr_3V_2O_8$, probably containing undetected vanadium oxide, which results from an insufficient reduction, for example, at 1000°C for 1 hr, as we have observed (cf. Fig. 5).

TABLE I

LIST OF INTERPLANAR SPACINGS, *h k l* INDICES, AND RELATIVE INTENSITIES OF $SrVO_{2.88}$

d_{obsd}(Å)	*h k l*	I/I_{max}
3.862	1 0 0	2
2.727	1 1 0	100
2.225	1 1 1	22
1.926	2 0 0	50
1.723	2 1 0	3
1.572	2 1 1	51
1.361	2 2 0	33
1.283	3 0 0	2
1.230	3 1 0	28
1.160	3 1 1	10
1.111	2 2 2	15
1.067	3 2 0	2

TABLE II

LIST OF INTERPLANAR SPACINGS, *h k l* INDICES, AND RELATIVE INTENSITIES OF $SrVO_{3.00}$

d_{obsd}(Å)	*h k l*	I/I_{max}
3.837	1 0 0	2
2.714	1 1 0	100
2.217	1 1 1	23
1.920	2 0 0	49
1.717	2 1 0	3
1.568	2 1 1	48
1.358	2 2 0	32
1.280	3 0 0	2
1.215	3 1 0	27
1.158	3 1 1	10
1.109	2 2 2	15
1.065	3 2 0	2

In conclusion, $SrVO_3$ can be synthesized as a pure phase only by annealing the sample under H_2 atmosphere at 1000°C for several hours.

2. *Study of* Sr_2VO_4

After intermediate firing in air, the powder is mainly constituted by hydroxylapatite $Sr_{10}(VO_4)_6(OH)_2$ with $Sr(OH)_2 \cdot H_2O$ and $SrCO_3$.

The H_2-annealed sample presents an X-ray pattern almost identical with Sr_2TiO_4 (structure K_2NiF_4): this has been indentified as Sr_2VO_4 which appears nearly pure on the diffractogram with traces of strontium oxide SrO, strontium hydroxide $Sr(OH)_2 \cdot H_2O$, and probably $SrVO_3$, not detectable because its main spectrum lines are hidden by these of Sr_2VO_4 (cf. Fig. 6). The compound Sr_2VO_4 is black.

High purity hydrogen is required to syn-

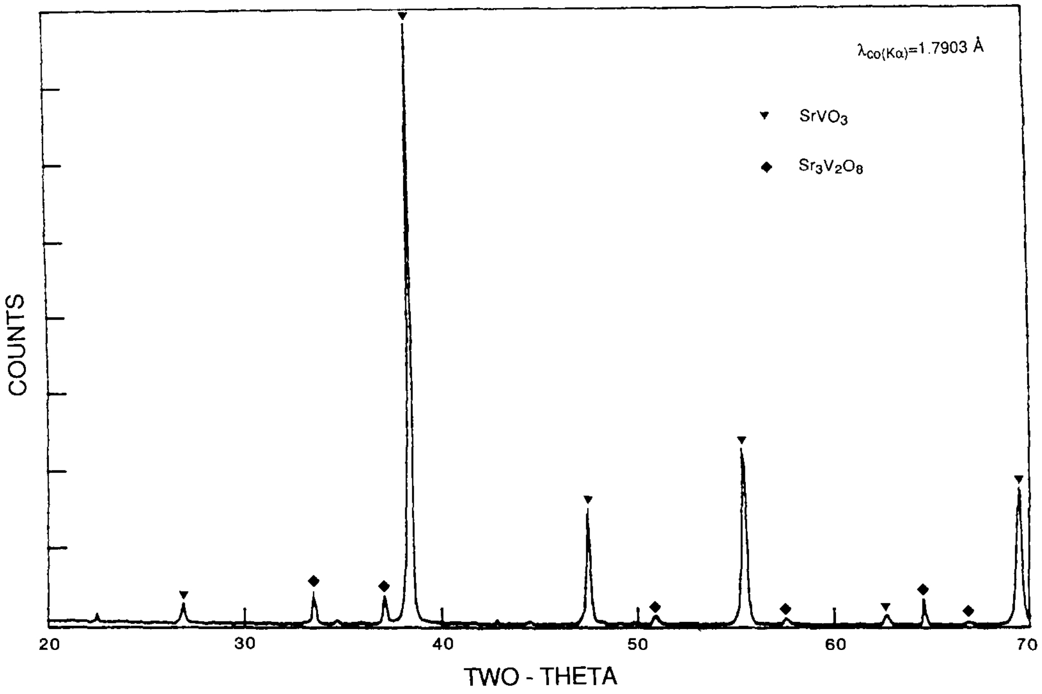

FIG. 5. Sr/V = 1: X-ray diffraction pattern of the H_2-annealed sample (1000°C—1 hr).

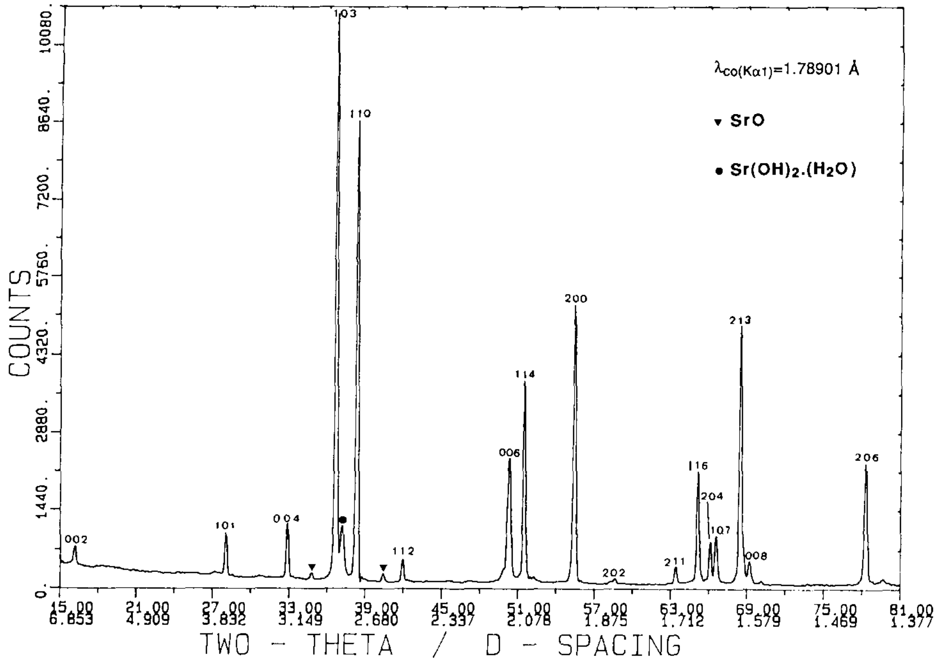

FIG. 6. Sr/V = 2: X-ray diffraction pattern of the H_2-annealed sample (1000°C—48 hr).

TABLE III

List of Interplanar Spacings, *h k l* Indices, and Relative Intensities of Sr_2VO_4

d_{obsd}(Å)	*h k l*	I/I_{max}
6.349	0 0 2	4
3.686	1 0 1	7
3.158	0 0 4	11
3.840	1 0 3	100
2.722	1 1 0	82
2.498	1 1 2	4
2.102	0 0 6	36
2.058	1 1 4	33
1.921	2 0 0	54
1.828	2 0 2	2
1.702	2 1 1	3
1.661	1 1 6	20
1.639	2 0 4	8
1.630	1 0 7	9
1.590	2 1 3	51
1.574	0 0 8	2
1.416	2 0 6	30

TABLE IV

Positional and Thermal Parameters for Sr_2VO_4

Atom	Position	*x*	*y*	*z*	B_{eq}(Å^2)
Sr	4*e*	0	0	0.35438(25)	0.25(10)
V	2*a*	0	0	0	0.3 not refined
O_I	4*c*	0	$\frac{1}{2}$	0	0.38(10)
O_2	4*e*	0	0	0.15778(28)	0.40(10)

TABLE V

Interatomic Distances (Å) for Sr_2VO_4

Sr–V(×4)	3.271(14)
Sr–O_I(×4)	2.650(17)
Sr–O_2(×4)	2.715(3)
Sr–O_2(×1)	2.477(26)
V–O_I(×4)	1.917(2)
V–O_2(×2)	1.986(24)
O_I–O_I(×4)	2.711(2)
O_I–O_2(×4)	2.760(16)

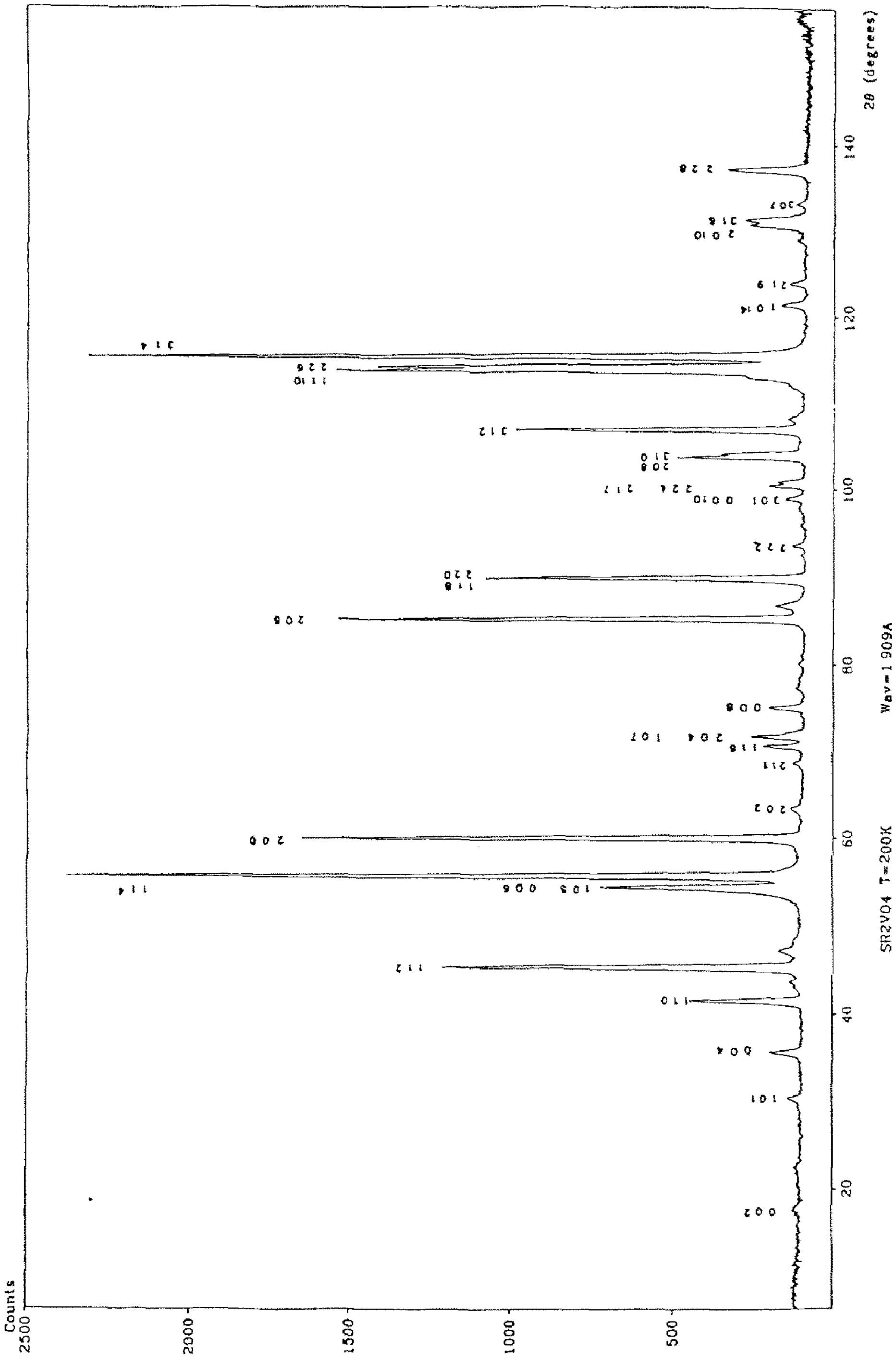

FIG. 7. Neutron diffraction diagram of Sr$_2$VO$_4$.

thesize pure Sr_2VO_4. It cannot be prepared by an industrial mixture of N_2 + 10% vol. H_2 at 1000°C. Oxygen and water traces present in the diluted hydrogen destabilize the valency IV state of vanadium compound in the Sr_2VO_4 structure. However, $SrVO_3$ can be synthesized in such a gas.

Sr_2VO_4 cristallizes in a tetragonal unit cell, space group I4/*mmm* with $a = b =$ 3.837(1) Å and $c =$ 12.576(3) Å. A list of interplanar spacings, *h k l* indices, and relative intensities is presented in Table III.

Neutron diffraction experiments permit the calculations of atomic positions and interatomic distances in the cell (cf. Tables IV and V). Cell parameters, determined from neutron diffraction measurements at 200 K, are $a = b =$ 3.8340(4) Å and $c =$ 12.587(13) Å. (cf. Fig. 7).

Physical Properties

We recall here the principal results reported in a previous publication (*4*). $SrVO_3$ oxide is a metallic conductor and exhibits Pauli paramagnetic behavior (*2, 5*). Sr_2VO_4 compound presents the same physical properties as La_2CuO_4: it is metallic and antiferromagnetic below 10 K (*4*).

To be able to make Sr_2VO_4 insulating and possibly a superconductor, it would be necessary to substitute monovalent ions for strontium. A lamellar structure would also be formed with vanadium ions in the mixed valency IV/V. All attempts to dope Sr_2VO_4 were not successful.

Acknowledgments

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