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Properties of a New Perovskite Oxyde Sr_2VO_4

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We have synthesized a new perovskite of the K_2NiF_4 structure Sr_2VO_4. The formal valence of vanadium is 4^+. We have performed X-ray and neutron experiments which show that the octahedra surrounding the vanadium is elongated. The compound is insulating and antiferromagnetic. These properties are reminiscent of those of La_2CuO_4 which becomes a high T_c superconductor when doped, the copper d^9 ion being replaced by the vanadium d^1 ion. © 1990 Academic Press, Inc.

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Since the discovery by Bednorz and Muller (*1*) of a perovskite type structure which shows superconductivity at temperatures well above those of conventional superconductors, interest has grown very much in that type of compounds. As it is believed, at least for the copper based one, that the layered structure is of primordial importance, those materials with this structure (*2*) seem particularly interesting. Recently a comparative study of the magnetic and electrical properties of perovskite oxides of K_2NiF_4 structure has been done (*3*). We have been interested in growing new perovskite oxides with a d^1 cation replacing the d^9 copper cation of the high T_c materials. The preparation and properties of perovskite type metavanadate $CaVO_3$ and $SrVO_3$ have already been reported (*4*). They are both metallic conductors and exhibit Pauli paramagnetic behavior. These perovskites do not present localization of the d^1 electron. The only attempt that we have found in the literature for a d^1 ion in the K_2NiF_4 structure is the synthesis of strontium orthoniobate Sr_2NbO_4 (*5*). However, we have been unable to synthesize it as the perovskite $Sr(Sr_{1/3}Nb_{1/3})O_3$ (*6*) seems to be stable enough to prevent its formation. Thus, we have tried another cation and report here our work on a new material Sr_2VO_4 that we have synthesized.

Experimental

The powder was prepared in the following way. The starting materials were V_2O_5 and $Sr(NO_3)_2$. We calcinated them under air and obtained near 800°C mainly hexagonal hydroxylapatite $Sr_{10}(VO_4)_6(OH)_2$ (HAP).

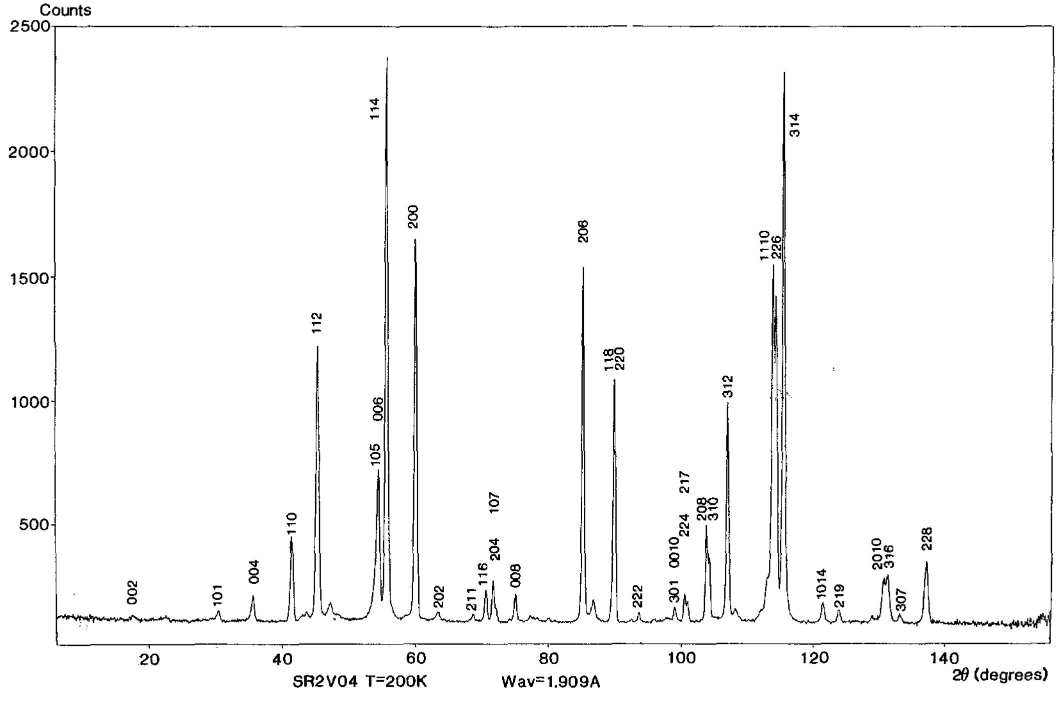

FIG. 1. Neutron diffraction diagram.

TABLE I

POSITIONNAL AND THERMAL PARAMETERS

Atom	Position	X	Y	Z	$B_{EQU.}$ (Å^2)
Sr	4e	0	0	0.35438(25)	0.25(10)
V	2a	0	0	0	0.3 not refined
O_1	4c	0	$\frac{1}{2}$	0	0.38(10)
O_2	4e	0	0	0.15778(28)	0.40(10)

We then reduced the compounds at 1000°C under dried hydrogen for 4 hr. Sr_2VO_4 was obtained as a black powder with $SrCO_3$ and $Sr(OH)_2 \cdot H_2O$.

Crystallographic Structure

The crystallographic structure of Sr_2VO_4 was determined by X-ray diffraction at room temperature. It belongs to the tetragonal group $I4/mmm$ and is isostructural with $Sr_2TiO_4(K_2NiF_4)$.

Neutron diffraction experiments were carried out, in order to obtain accurately the oxygen positions, at the Institut Laüe Langevin using D1A, powder diffractometer at two temperatures, $T = 5$ and 200 K (Fig. 1).

The atomic positions and thermal parameters were refined using the Rietvield analyses profile method (7). The reliability factor is $R = \frac{\Sigma\, |I_{\text{obs}} - I_{\text{cal}}|}{\Sigma\, I_{\text{obs}}} = 8\%$. The weak parasitic lines of the compound $Sr(OH)_2 \cdot H_2O$ did not permit refinement of the anisotropic thermal parameters (Table I).

The lattice parameters at $T = 200$ K are

$$a = b = 3.8340(4)\ \text{Å}, \quad c = 12.5874(13)\ \text{Å}.$$

The interatomic distances are reported in Table II and the list of the calculated intensities is reported in Table III.

At low temperature $T = 5$ K no magnetic contribution is obvious; it is noteworthy that a magnetic moment $\leq 0.6\ \mu B$ cannot be detected with our measurements.

TABLE II

INTERATOMIC DISTANCES (Å)

Sr–V (×4)	3.271(14)
Sr–O_1 (×4)	2.650(17)
Sr–O_2 (×4)	2.175(3)
Sr–O_2	2.477(26)
V–O_1 (×4)	1.917(2)
V–O_2 (×2)	1.986(24)
O_1 – O_1 (×4)	2.711(2)
O_1 – O_2 (×4)	2.760(16)

Physical Properties

With compact powder, we have performed electrical measurements between room temperature and liquid helium temperature. The behavior is that of the insulating type (Fig. 2). This is consistent with the general behavior of the A_2BO_4 oxide compared to the ABO_3 pervoskite.

TABLE III

OBSERVED AND CALCULATED INTENSITIES AT $T = 200$ K

H	K	L	I_{CAL}	I_{OBS}	H	K	L	I_{CAL}	I_{OBS}
0	0	2	409	284	3	0	1	100	321
1	0	1	457	603	0	0	10	427	701
0	0	4	952	1,224	2	2	4	924	904
1	0	3	56	32	2	1	7	630	646
1	1	0	3,422	3,634	3	0	3	54	66
1	1	2	12,560	11,784	2	0	8	3,110	3,008
1	0	5	433	1,200	3	1	0	2,078	2,119
0	0	6	5,795	7,039	3	1	2	8,104	7,915
1	1	4	22,331	22,072	1	1	10	13,022	14,548
2	0	0	13,015	14,786	3	0	5	207	216
2	0	2	142	496	2	2	6	10,295	11,206
2	1	1	287	358	3	1	4	20,929	21,221
1	1	6	1,212	1,243	1	0	11	957	963
2	0	4	1,235	1,394	2	1	9	617	564
1	0	7	361	441	3	2	1	257	364
2	1	3	69	75	2	0	10	1,851	2,040
0	0	8	1,045	1,035	3	1	6	1,907	1,646
2	1	5	438	464	0	0	12	1,166	988
2	0	6	12,216	11,409	3	0	7	368	423
1	1	8	367	637	3	2	3	166	No
2	2	0	7,681	8,314	2	2	8	3,622	3,312
2	2	2	81	123	3	2	5	697	875
1	0	9	347	387	1	1	12	126	203

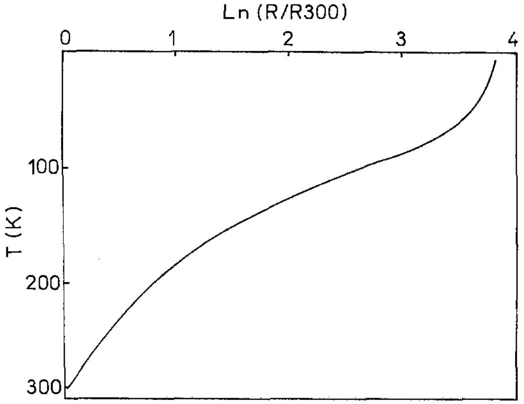

FIG. 2. Electrical measurements.

We have measured the magnetic susceptibility which exhibited antiferromagnetism below 10 K (Fig. 3). Above T_N, the susceptibility can be fitted with a Curie–Weiss Law and a Curie paramagnetic temperature of 7–5 K. The value of the Néel temperature is very sample dependent. On some samples we have measured a Néel temperature as high as 100 K. We have not been able to observe antiferromagnetism with polarized neutrons. However, we note that a moment smaller than one Bohr magneton is difficult to observe. La_2NiO_4 is known to be antiferromagnetic (*8*). However, only recently has it been confirmed by neutron experiments. Antiferromagnetism of La_2CuO_4 has also been very difficult to observe by neutron scattering.

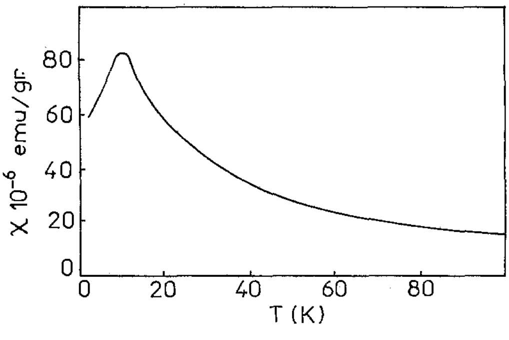

FIG. 3. Magnetic measurements.

Discussion

The aim of our work was to realize an antiferromagnet with spin one-half. Indeed, just after the discovery of high T_c superconductors, Anderson (*9*) pointed out a possible relationship between superconductivity and a spin one-half antiferromagnet. One of us has developped (*10*) a theory of superconductivity for a spin one-half doped Mott insulator and applied it to La_2CuO_4. In such a theory a d^9 cation is equivalent to a d^1. Thus we synthesized a compound similar to La_2CuO_4 but with the d^1 cation.

There are, however, two main differences. The first one, and probably the most important here, is that the oxygen *p* band is well below the *d* band contrary to La_2CuO_4. In the latter compound the oxygen band is close to the *d* band and when doped the holes are mainly on oxygen. We have performed (*11*) band structure calculations for this material which prove these results. The second difference is that the electron in Sr_2VO_4 is in a *t2g* state instead of being in the *eg* band as in the copper compound. Moreover, the distortion of the octahedron around the cation is smaller in our compound that in the copper one, which means that the degeneracy of the state is not completely lifted.

Our next step was to dope our compound in order to make it metallic and possibly superconducting. This would be an interesting test, whether the position of the *p* band of the oxygen is crucial for superconductivity. However, we have not succeeded in substituting an alkaline ion into the structure and thus are unable to give on experimental answer to the question of the effect of the oxygen band.

Acknowledgments

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