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On the Electrical Properties of Polycrystalline Delafossite-Type $AgNiO_2$

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$AgNiO_2$ is prepared by reaction of molten silver nitrate with $NaNiO_2$. Powder X-ray diffraction shows that the compound has the delafossite structure of space group $R\bar{3}m$. Magnetic data give evidence for the localization of the 3*d*-electrons of most Ni atoms. Electrical conductivity and thermoelectric measurements performed between 4.2 and 300 K on polycrystalline samples show that $AgNiO_2$ behaves like a semimetal. *N*-type and *p*-type charge carriers are created by a slight overlapping of the *d* band of silver atoms with the σ^* antibonding band resulting from the overlapping of the Ni 3*d*- and O 2*p*-orbitals.

Introduction

Delafossite-type compounds of general formula $A^{+}B^{3+}O_2$ are of large interest both from the basic and the applied point of view. $CuCrO_2$, for instance, exhibits catalytic properties for the synthesis of methanol (*1*) and $AgNiO_2$ has been proposed as electrode material for Zn-air batteries (*2*). Despite such worthwhile features only few investigations have been devoted to the physical properties of delafossite compounds especially when the monovalent cation A is silver. Only one previous publication could be found on $AgNiO_2$; it concerned preparation, chemical characterization, and structural determination by electron diffraction (*3*). This lack of data on $AgNiO_2$ might be ascribed, at least partly, to the difficulties of preparation which requires relatively mild conditions due to weak thermal stability of the material. However the relatively high value of electrical conductivity and its temperature dependence which differ from all other so far known Cu and Ag delafossite-type compounds prompted us to carry out the present study. Some preliminary results are reported here on polycrystalline samples.

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TABLE I

CHEMICAL COMPOSITION OF THE $AgNiO_2$ SAMPLE

	Theor. composition weight %	Exp. composition weight %		TGA under H_2/N_2
		Results[a]	Average	
Ag	54.32	54.17 53.78	53.97	
Ni	29.56	29.35 29.35 29.53	29.41	
O	16.16		16.28[b]	16.39[c] 16.15[d] 16.07[e]
Na	0	0.22 0.34 0.26	0.27	
N	0	0.07 0.06	0.07	

[a] Results obtained from the Service Central d'Analyse du CNRS by plasma emission spectroscopy.

[b] Determined by difference.

[c] Assuming that the total weight loss is only due to reaction (1).

[d] Taking into account volatilization of a Na-containing impurity (e.g., Na_2O oxide).

[e] Taking into account volatilization of a N-containing impurity.

Sample Preparation and Characterization

Polycrystalline $AgNiO_2$ has been prepared by exchange reaction between $NaNiO_2$ and $AgNO_3$ with the molar ratio 1 : 1.3. We have observed that such an excess of silver nitrate prevents the formation of a small amount of silver metal which had been detected by X-ray diffraction for a stoichiometric ratio of reactants. The starting mixture was finely ground and compacted in an argon dry box. The obtained pellets were put into a silica tube which was sealed in vacuum (10^{-5} bar) and heated for 4 days at 250°C. After this thermal treatment X-ray diffraction shows that in addition to $AgNiO_2$ and $NaNO_3$ the sample contains some traces of $NaNO_2$. Sodium compounds were removed after leaching the ground sample with alcohol and water. Washing was performed in darkness in order to avoid eventual formation of Ag-metal and repeated until no more sodium could be detected by flame spectroscopy.

Chemical composition was determined by emission spectroscopy at the Service Central d'Analyse du CNRS. The comparison between experimental and theoretical weight rates supplied in Table I shows that the sample is stoichiometric in the limit of the experimental errors.

TGA carried out under oxygen flow shows that the weight begins to decrease at 610 K. The weight loss corresponds to the decomposition reaction: $AgNiO_2 \rightarrow Ag + NiO + \frac{1}{2} O_2^{\nearrow}$. The well-known nonstoichiometry of nickel oxide prevents an accurate determination of the oxygen content in the sample. In order to obtain a quantitative determination of the oxygen content we performed TGA under H_2 (10%)/N_2 flow. The reduction corresponding to the reaction

$$AgNiO_2 + 2H_2 \rightarrow Ag^0 + Ni^0 + 2H_2^{\nearrow}O \quad (1)$$

begins at ≃385 K and was carried out at constant temperature. A further increase of temperature up to 925 K gives rise to a small additional weight loss attributed to volatilization of sodium oxide as traces of sodium were detected analytically. The weight loss confirms the stoichiometric composition of the sample and reveals an oxygen content very close to that determined by difference (Table I).

The Ni oxidation state has been confirmed by iodometric titration. The amount of iodine released during the reaction has been determined by thiosulfate. The average oxidation state of nickel was found to be 3 ± 0.02, in agreement with the chemical composition.

The powder X-ray diffraction data were obtained using a copper anticathode and KCl as an internal standard. X-ray diffrac-

TABLE II

LATTICE PARAMETERS AND DENSITY OF $AgNiO_2$

	Lattice parameters		Density	
Samples	a (Å)	c (Å)	Exp.	Theor.
This work	2.936	18.35	7.109	7.218
Bityutskii and Khitrova (*3*)	2.94	18.52	6.86	7.19

TABLE III

X-RAY POWDER DATA OF $AgNiO_2$

$h\ k\ l$	d_{calc}	d_{obs}	Int.[a]
0 0 3	6.1167	6.1381	vw
0 0 6	3.0586	3.0583	s
1 0 1	2.5188	2.5232	w
0 1 2	2.4505	2.4551	vs
1 0 4	2.2241	2.2278	s
0 0 9	2.0391	2.0411	w
1 0 7	1.8253	1.8251	vw
0 1 8	1.7033	1.7025	w
0 0 12	1.5293	1.5294	w
1 0 10	1.4881	1.4878	w
1 1 0	1.4681	1.4671	w
1 1 3	1.4276	1.4277	vw
1 1 6	1.3235	1.3232	w
0 2 1	1.2684	1.2677	vw
2 0 2	1.2594	1.2601	w
0 2 4	1.2252	1.2249	vw
1 1 9	1.1914	1.1899	vw
0 1 14	1.1651	1.1647	vw
0 2 8	1.1120	1.1118	vw
1 1 12	1.0591	1.0592	vw
0 2 10	1.0451	1.0459	w
0 1 17	0.9937	0.9947	vw
1 2 2	0.9559	0.9462	vw
2 1 4	0.9407	0.9403	vw

[a] s, strong; vs, very strong; w, weak; vw, very weak.

tion patterns show that $AgNiO_2$ has the $3R$ delafossite-type structure characterized by $R\bar{3}m$ space group.

The delafossite structure consists of close-packed oxygen double layers in which the octahedral sites are occupied by the B^{3+} cations. These oxygen sheets are linked by monovalent A^+ ions with a twofold linear coordination. Each A atom is surrounded by six nearest neighbors located in a plane perpendicular to the hexagonal c-axis.

The lattice parameters given in Table II are in agreement with the previous results of Bityutskii and Khitrova (*3*). The d-spacings and the corresponding hkl indices are reported in Table III.

The density of our sample has been determined using a hydrostatic method described elsewhere (*4*). The experimental value is close to that calculated on the base of three formula units in the unit cell (Table II).

Electrical Properties

Electrical resistivity measurements have been carried out in the temperature range 4–300 K on polycrystalline materials using the colinear four-probe method and automatic equipment described elsewhere (*5*). The thermal variation of the resistivity shown in Fig. 1 illustrates a metallic behavior when $d\rho/dT$ is positive for $20 < T < 300$ K. Below 20 K the resistivity increases slightly as the temperature decreases. However, it may be noticed that the experimental values are relatively high ($0.065 \leq \rho \leq 0.01\ \Omega \cdot \text{cm}$) for a classical metal.

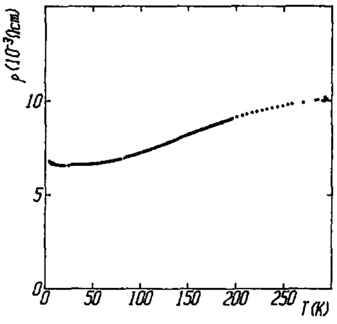

FIG. 1. Electrical resistivity of $AgNiO_2$.

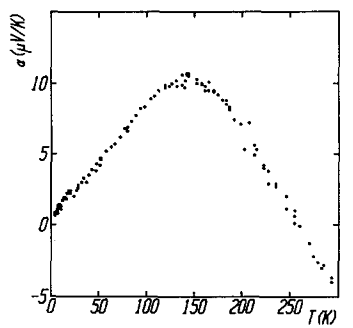

FIG. 2. Thermoelectric power of $AgNiO_2$.

The Seebeck coefficient α has been measured in the temperature range 4–300 K using homemade equipment previously described (*6*). At rising temperature α increases linearly with temperature up to a maximum value $\alpha_{max} = +10\ \mu V/K$ at $T =$ 150 K (Fig. 2). For $T > 150$ K the Seebeck coefficient decreases and becomes finally negative for $T \geq 260$ K.

Discussion

Energy Diagram

Taking into account the linear twofold coordination of silver and some well-known general features of the linear complexes of d^{10} cations, Rogers *et al.* (*7*) have proposed a band diagram for ABO_2 delafossite. This diagram can explain the insulating character of the previously studied Cu and Ag (d^{10}) delafossites as well as the metallic behavior of the Pd and Pt (d^9) delafossites. The latter can be ascribed to the delocalization of carriers partially occupying the band issued from the highest d-orbitals of the A cations.

Nevertheless, such an energy diagram cannot account for the metallic-type behavior observed for our $AgNiO_2$ samples (Figs. 1 and 2) unless a large enough deficiency of silver atoms could give rise to a significant hole concentration in the Ag-4d band. However, in such a case the thermopower α would be mainly due to extrinsic p-type carriers, as no thermal excitation of intrinsic carriers could be detected in the thermal variation of resistivity (Fig. 1). Therefore α should remain positive in the investigated temperature range and should have a large value corresponding to a small carrier number in agreement with the chemical analysis which shows that the composition cannot differ significantly from the stoichiometry.

Origin of the Charge Carriers

Above 400 K $AgNiO_2$ is paramagnetic and follows a Curie–Weiss law with $C =$ 0.65 emu CGS K mole^{-1}[1] and $\theta_p = -140$ K. Below 400 K the magnetization M is no longer rigorously proportional to the field H, exhibiting a small ferromagnetic-like component.[2] The slope of the apparent reciprocal susceptibility H/M vs temperature is about 0.38 emu CGS K mole^{-1}.

A model assuming high-spin (HS) configuration with a localization of the t_{2g} Ni-electrons accounting for the magnetic properties and a delocalization of the e_g-electrons, leading to metallic-type behavior of the resistivity above 20 K, must be excluded as:

(i) to our knowledge HS configuration has never been observed in Ni^{3+} oxides, with the exception of $BaLaNiO_4$ (*8*);

(ii) the Ni–O distance is 1.94 Å (*3*), a value which is exactly the sum of the ionic radii of O^{2-} in fourfold coordination ($r^{IV}_{O^{2-}} =$ 1.38 Å) and of Ni^{3+} in low-spin (LS) config-

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[1] This Curie constant is much higher than the spin-only value normally expected for Ni^{3+} with a low-spin configuration ($C = 0.375$ emu CGS K mole^{-1}). However, a large value is observed for most nonmetallic nickelates (III) such as $YNiO_3$ ($C = 0.63$ emu CGS K mole^{-1}), $LuNiO_3$ ($C = 0.66$) (*11*), and $LiNiO_2$ ($C =$ 0.74) (*12*). Only $NaNiO_2$ seems to have a Curie constant ($C = 0.386$) closer to the theoretical value (*13*).

[2] A similar behavior has been reported for $LiNiO_2$ which is no longer paramagnetic below 210 K (*12*). A more detailed study of this feature of $AgNiO_2$ will be published elsewhere.

uration ($r^{VI}_{Ni^{3+}_{LS}} = 0.56$ Å against $r^{VI}_{Ni^{3+}_{HS}} = 0.60$ Å) according to Shannon's Table (*9*);

(iii) the sign of the thermoelectric power changes at 260 K;

(iv) a wide ESR line ($\Delta H_{pp} \simeq 1000$ G) has been observed for a $AgNiO_2$ sample prepared from $LiNiO_2$ and exhibiting a higher resistivity. The *g* value at room temperature (2.24) seems to exclude an HS state (*10*).

Therefore, we can conclude that in $AgNiO_2$, Ni^{3+} has a LS configuration and that the e_g^1-electrons of most Ni atoms are localized.

Delocalization of extrinsic either "Ni^{4+}" holes or "Ni^{2+}"-electrons in the Ni^{3+}-planes cannot be considered to be the prevailing mechanism of the electrical conductivity for reasons similar to those given for eventual presence of holes in the silver band. Such a mechanism involving a departure from the stoichiometry which in any case cannot exceed the limits allowed by the chemical analysis could not account in particular for the observed change of thermoelectric power sign at $T = 260$ K.

Our $AgNiO_2$ sample can rather be considered to be a semimetal on hand of the localization of most Ni *d*-electrons, the electrical conductivity being much lower than that of normal metal[3] and sign change at 260 K of the thermoelectric power.

A simple model may explain these results: the localization of the Ni^{3+} *d*-electrons implies that the σ^* band due to overlapping of the e_g-orbitals through σ-bonding with oxygen 2*p*-orbitals is split into a fully occupied σ^{*1} band and an empty σ^{*2} band separated by the U' intraatomic energy according to the usual model now generally accepted for *d*-electrons of transition element oxides (*14*). Here we assume that the e_g-levels remain degenerated, since no cooperative Jahn–Teller effect seems to give rise to any significant crystallographic distortion. The carriers could result from a slight overlapping of the bottom of the (empty) σ^{*2} band with the upper part of the 4*d*-band of silver as illustrated in Fig. 3. From a chemical point of view such a phenomenon can be written as $Ag^+ + Ni^{3+} \rightleftarrows$ "Ag^{2+}" $+ Ni^{2+}$, the equilibrium being, of course, strongly shifted toward the left-hand side.

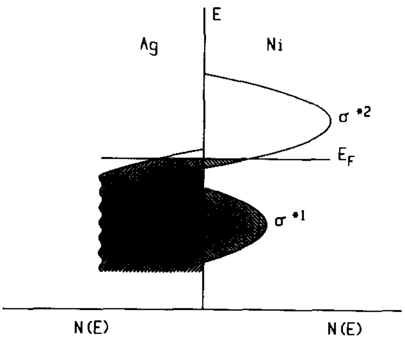

FIG. 3. Schematic density of states vs energy diagram showing splitting of the σ^* band and overlapping with 4*d* band of silver. (σ^* results from the overlapping of Ni e_g-orbitals and O 2*p*-orbitals).

In the scope of this model it seems easy to understand the differences observed in the electrical behavior of $AgNiO_2$, $LiNiO_2$, and $AgCoO_2$: $LiNiO_2$ is an insulator with a thermally activated conductivity as no possibility of carrier creation can result from a band overlapping. In $AgCoO_2$, Co^{3+} has a low-spin configuration (at least up to 650 K) (*15*). The insulating character of $AgCoO_2$ can be understood thanks to the fact that the σ^* band of Co^{3+} lies at an energy level higher than that of Ni^{3+}, which corresponds to an oxidizing power smaller for Co^{3+} than for Ni^{3+}.

Conclusion

The investigation of the electrical properties of $AgNiO_2$ has shown that this delafos-

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[3] This result could be attributed to the resistance of the grain boundaries which in any way represents a part of the resistivity values reported here. However, pellets of polycrystalline $PdCrO_2$ prepared under similar conditions exhibit an electrical conductivity one order of magnitude higher.

site-type compound has the behavior of a semimetal. Magnetic measurements show evidence of the localization of the majority of the Ni *d*-electrons. *N*-type and *p*-type charge carriers result from the slight overlapping of the *d*-band of silver and the σ^* nickel–oxygen antibonding band.

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References

1. J. R. Monnier, M. J. Hanrahan, and G. Apai, *J. Catal.* **92,** 119 (1985).
2. RAY O Vac Co., *Japan Kokai Tokkyo Koho,* 8276, 754; 8276, 756; 8276, 757.
3. P. N. Bituitskii and V. I. Khitrova, *J. Struct. Chem.* **9,** 921 (1968) (translation of *Z. Strukt. Khimii* **9,** 1034 (1968)).
4. L. Rabardel, M. Pouchard, and P. Hagenmuller, *Mater. Res. Bull.* **6,** 1325 (1971).
5. P. Dordor, E. Marquestaut, C. Salducci, and P. Hagenmuller, *Rev. Phys. Appl.* **20,** 795 (1985).
6. P. Dordor, E. Marquestaut, and G. Villeneuve, *Rev. Phys. Appl.* **15,** 1607 (1980).
7. D. B. Rogers, R. D. Shannon, C. T. Prewitt, and J. L. Gillson, *Inorg. Chem.* **10,** 723 (1971).
8. G. Demazeau, J. L. Marty, B. Buffat, J. M. Dance, M. Pouchard, P. Dordor, and B. Chevalier, *Mater. Res. Bull.* **17,** 37 (1982).
9. R. D. Shannon, *Acta Crystallogr. Sect. A* **32,** 751 (1976).
10. J. M. Dance, private communication.
11. G. Demazeau, A. Marbeuf, M. Pouchard, and P. Hagenmuller, *J. Solid State Chem.* **3,** 582 (1971).
12. K. Hirakawa, H. Kadovaki, and K. Ubukoshi, *J. Phys. Soc. Japan.* **54,** 3256 (1985).
13. P. F. Bongers and N. Enz, *Solid State Commun.* **4,** 153 (1966).
14. J. B. Goodenough, *Prog. Solid State Chem.* **5,** 145 (1972).
15. J. P. Doumerc, A. Wichainchai, A. Ammar, M. Pouchard, and P. Hagenmuller, *Mater. Res. Bull.* **21,** 745 (1986).