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Nickel Supermixed Valence in Stoichiometric $BaNi_{0.83}O_{2.5}$

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Single crystals of $BaNi_{0.83}O_{2.5}$ were grown from mixtures of $BaCO_3$ and NiO using KOH as a flux. The composition and the crystal structure have been established from X-ray single crystal diffraction data. $BaNi_{0.83}O_{2.5}$ is stoichiometric and crystallizes in a trigonal structure, space group $R32$, with hexagonal unit-cell parameters (Å) a = 9.8890(4) c = 12.867(4), volume 1089.7(3) Å^3, and Z = 18. $BaNi_{0.83}O_{2.5}$ contains two kinds of Ba atoms both coordinated with 10 oxygens, and three different Ni atoms octahedrally coordinated to oxygen at distances which approximately correspond to Ni^{2+} and to low spin Ni^{3+} and Ni^{4+}. NiO_6 octahedra share opposite faces giving rise to chains parallel to the c axis, in which some Ni–Ni distances are shorter than in Ni metal. This structure, which is compared with that of $BaNiO_3$, can be considered like a close packing of Ba and oxygen atoms in which almost one quarter of the octahedral sites are occupied by nickels. $BaNi_{0.83}O_{2.5}$ is an electrical insulator. The results of magnetic measurements from room temperature to 5 K are given. © 1994 Academic Press, Inc.

INTRODUCTION

Some of the oxides of nickel, barium, and rare earths that we have studied (1–3) contain chains of flattened NiO_6 octahedra with short Ni–O–Ni distances (about 3.76 Å) and nearest oxygens to Ni distorted from the 90° angles of a regular octahedron. This justifies the one-dimensional antiferromagnetic behavior (2) of these oxides and has been shown to be understandable (4) using a theoretical model which combines various results and arguments. Because of our interest in the interactions present in these monodimensional compounds we decided to turn our attention to the systems E–Ni–O, where E is an alkaline–earth metal. In this work we present the synthesis, the crystal structure and some properties of an oxide of Ni and Ba which, in spite of its apparently intricate composition, is stoichiometric.

EXPERIMENTAL SECTION

Crystal growth. $BaNi_{0.83}O_{2.5}$ single crystals were grown by several methods. The best results were obtained heating a mixture of reagent grade NiO, $BaCO_3$, and KOH in molar ratios Ni : Ba : K = 3 : 1 : 8 for 10 min. at 750°C in an inconel crucible, cooling at room temperature, reheating for 10 min at 1100°C, and turning off power to the furnace. The product was washed in distilled water several times, dried, and filtered. Small black prismatic crystals of $BaNi_{0.83}O_{2.5}$ were separated mechanically from the remaining compact powder using an appropriate sieve.

Crystal characterization. Examined by energy dispersive X-ray analysis, the $BaNi_{0.85}O_{2.5}$ crystals appeared to contain Ba and Ni and were free from K, Fe, and Cr. For this purpose a JEOL scanning microscope JSM-35 equipped with an energy-dispersive system KEVEX 7077 was employed. A QUANTUM DESIGN superconducting quantum interference device magnetometer operated under zero-field cooling conditions at various fields and a four-point probe method were used to perform the magnetic and resistive measurements. For these the sample was a small bar cut from a pellet consisting in extremely fine powdered crystals which was sintered at 1000°C for 30 min. For the magnetic measurements finely powdered crystals were employed.

Collection of X-ray diffraction data. A summary of the fundamental crystal data is given in Table 1. A black prismatic crystal was mounted in a kappa diffractometer. The cell dimensions were refined by least-squares fitting the θ values of 25 reflections. The R cell was determined from the systematic extinctions. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ni and Ba atoms were taken from the International Tables for X-Ray Crystallography (5). The space group $R32$ was obtained during the course of the structure solution after trying the hexagonal space groups in which the only extinction is $-\mathbf{h} + \mathbf{k} + \mathbf{l} = 3\mathbf{n}$.

Structure determination. The heavy atoms were lo-

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TABLE 1
Crystal and Refinement Data

Formula	$BaNi_{5/6}O_{5/2}$
Mr	226.3
Crystal system	trigonal
Space group	$R32$ (No. 155)
a, Å	9.8890(4)
c, Å	12.867(4)
V, Å^3	1089.7(3)
Z	18
$F(000)$	1788
ρ(calc), g cm^{-3}	6.21
temperature, °C	22
μ, cm^{-1}	224.3
Crystal dimensions, mm	0.05 × 0.05 × 0.01
Diffractometer	Enraf-Nonius CAD4
Radiation	graphite-monochromated Mo$K\alpha$ (λ = 0.71069 Å)
Scan technique	$\Omega/2\theta$
θ	$1 < \theta < 30$
Data collected	(0, 0, 0) to (13, 13, 18)
Unique data	415
Unique data (I) ≥ 3 σ(I)	199
R(int), %	6.8
Std. reflections	3/42
RF, %	4.5
R_wF, %	4.6
Average shift/error	0.36

cated from a three-dimensional Patterson map. The positions of the oxygen atoms were obtained from Fourier synthesis. An empirical absorption correction (6) was applied at the end of the isotropic refinement. The maximum and minimum absorption factors were 1.08 and 0.99 respectively. Anisotropic full-matrix least-squares refinement with unit weights led to $R = 0.045$ and $R_W = 0.046$. No trend in ΔF vs F_o or sin θ/λ was observed. Most of the calculations were carried out with the X-ray 80 system (7).

RESULTS AND DISCUSSION

A preliminary study of the crystals by X-ray diffraction techniques showed that among all the Ba and Ni oxides which are known (8–11), they could be related to one phase not completely characterized which was formulated (8) as $Ba_3Ni_3O_8$ or $BaNiO_{2.67}$ with hexagonal unit-cell parameters (Å) **a** = 5.72, **c** = 4.30 and some years later (9) obtained as the polycrystalline product of heating $BaNiO_{2.55}$ to 1100°C in air, showing rhombohedral symmetry and hexagonal lattice constants (Å) $\mathbf{a}' = 9.85 \simeq \sqrt{3}\mathbf{a}$, $\mathbf{c}' = 13.0 \simeq 3\mathbf{c}$. In particular, the X-ray powder diffraction pattern of our crystals was almost identical to that (8) of $BaNiO_{2.67}$.

Atomic position coordinates and temperature factors as well as main interatomic distances and angles for $BaNi_{0.83}O_{2.5}$ are included in Tables 2 and 3. Although the composition per unit-cell for the crystal studied is $Ba_{18}Ni_{15}O_{45}$ or $3(Ba_6Ni_5O_{15})$, as can be seen in Table I, the formula $BaNi_{0.83}O_{2.5}$ has been chosen in order to easily compare this oxide, where Ni shows a mean oxidation state of 3.6, with the remaining known oxides of Ba and Ni. In $BaNi_{0.83}O_{2.5}$ there are two kinds of Ba atoms, both coordinated with 10 oxygens at a mean distance of 2.85 Å, and three different Ni atoms octahedrally coordinated to oxygen. As a consequence, each oxygen atom is surrounded by four Ba and two Ni. Figure 1 shows a perspective of the unit cell as seen in the direction of the **ab** plane. The NiO_6 octahedra share opposite faces giving rise to chains parallel to the **c** axis, in which some Ni–Ni distances are shorter than in Ni metal (2.49 Å). The $Ni(1)O_6$ and $Ni(2)O_6$ octahedra are almost regular, whereas $Ni(3)O_6$ octahedra appear much more distorted. The sequence of the NiO_6 octahedra along the chain is Ni(3) Ni(2) Ni(1) Ni(1) Ni(2) as can be seen in Figure 2. The average distances of Ni(1), Ni(2), and Ni(3) to oxygen, 1.88, 1.96, and 2.14 Å respectively, approximately correspond (12) to Ni^{4+}, d^6 low spin, 1.88 Å; Ni^{3+}, d^7 low spin, 1.96 Å; and to Ni^{2+}, for which the mean of 70 compounds equals 2.065 Å, and values from 2.02 to 2.13 Å are known (13).

$BaNi_{0.83}O_{2.5}$ is the same compound formerly formulated as $BaNiO_{2.67}$ (8) and $BaNiO_x$ (9). In the last work (9) the authors prepared polycrystalline samples of $BaNiO_x$ and chose an oxygen-deficient unit-cell related to that of hexagonal $BaNiO_3$ (**a** = 5.631 Å, **c** = 4.808 Å) with $\mathbf{a}' = 9.85 \simeq \sqrt{3}\mathbf{a}$ and $\mathbf{c}' = 13.0 \simeq 3\mathbf{c}$. After assuming a trigonal R-type cell, S.G. $R3c$, the composition $BaNiO_{2.5}$ and statistical occupation of Ni and oxygen sites, they obtained the R factor of 0.13. The present refinement of single-crystal data in the S.G. $R32$ has led to an acceptable R value, 0.045, anisotropic thermal factors for the heavy atoms, and integers for the population factors not only of the metals but also of the oxygens. This contrasts with the fractionary and exceedingly low values, 0.375 and 0.417, for the population factors of Ni and oxygen atoms respectively, obtained using the $R3c$ space group (9). As a consequence, the molar ratio Ba : Ni results precisely defined, Ba : Ni = 1.20, and on the other hand, the oxygen stoichiometry equals 2.5 atoms per Ba atom. Finally, a thorough examination of the diffraction data shows that reflexions like 0.0.9 and 0.0.15, incompatible with a **c** plane, although weak, are clearly present.

The crystal structure of $BaNi_{0.83}O_{2.5}$ can be compared with that (4) of $BaNiO_3$. Both oxides contain chains of NiO_6 octahedra with short Ni–Ni distances. The main difference between the two structures lies in the kind of their Ni atoms: in $BaNiO_3$ all of them are crystallographically equivalent, whereas in $BaNi_{0.83}O_{2.5}$ there exists three different nickels.

TABLE 2
Final Atomic Coordinates and Thermal Parameters for $BaNi_{0.83}O_{2.5}$ ($\times 10^3$ Å^2) with ESDs in Parentheses

Atom	Sites	x/a	y/b	z/c	U_{eq}
Ba(1)	9*d*	0.3285(13)	0.0000(0)	0.0000(0)	25(4)
Ba(2)	9*e*	0.6555(10)	0.0000(0)	0.5000(0)	14(3)
Ni(1)	6*c*	0.0000(0)	0.0000(0)	0.0994(27)	21(6)
Ni(2)	6*c*	0.0000(0)	0.0000(0)	0.2812(18)	10(6)
Ni(3)	3*b*	0.0000(0)	0.0000(0)	0.50000(0)	48(10)
O(1)	18*f*	0.5151(59)	0.1716(51)	0.5165(29)	17(0)
O(2)	9*d*	0.1377(68)	0.1377(68)	0.0000(0)	17(0)
O(3)	18*f*	0.3432(52)	0.5247(52)	0.0442(27)	17(0)

Atom	U11	U22	U33	U12	U13	U23
Ba(1)	26(6)	26(0)	22(10)	13(3)	−6(2)	−12(0)
Ba(2)	16(4)	5(0)	18(8)	3(2)	2(1)	4(0)
Ni(1)	17(0)	17(0)	30(19)	8(3)	0	0
Ni(2)	12(0)	12(0)	4(19)	6(3)	0	0
Ni(3)	68(0)	68(0)	8(28)	34(7)	0	0

To accomodate the sequences Ni(3) Ni(2) Ni(1) Ni(1) Ni(2), this oxide needs a unit-cell larger than that of $BaNiO_3$, a unit-cell with an **a** value, 9.889 Å, equal to that of $BaNiO_3$, 5.629 Å, multiplied by $\sqrt{3}$, and a **c** parameter which is not three times the **c** value for $BaNiO_3$ but the sum of Ni–Ni distances 2.81 + 2.34 + 2.56 + 2.34 + 2.81 = 12.86 Å. On the other hand the Ni–Ni distances in $BaNiO_3$, 2.41 Å, are shorter than the mean Ni–Ni distance in $BaNi_{0.83}O_{2.5}$, 2.51 Å, but this oxide contains some Ni atoms at distances as short as 2.34 Å.

$BaNi_{0.83}O_{2.5}$ and $BaNiO_3$ can be described as distorted hexagonal close packings of the Ba and oxygen atoms, with cell volumes per packed atom of 17.3 and 16.5 Å^3 respectively. In the ideal close packing all the Ba–O and O–O distances between the layers and between adjacent layers should be the same. Within the BaO_3 layers of $BaNiO_3$ (10) the O–O distance is either 2.47 or 3.16 Å and the Ba–O distance equals 2.82 Å, while the O–O distance between the layers is 2.76 Å. A partial view of the Ba_2O_5 layers perpendicular to **c** in $BaNiO_{0.83}O_{2.5}$ is shown in Fig. 3. Table 4 includes the distances less than 3.5 Å between packed atoms in $BaNi_{0.83}O_{2.5}$. The good number of these distances could be foreseen from and agree with the distortions of the NiO_6 octahedra. $BaNi_{0.83}O_{2.5}$ is less symmetrical and slightly less closely packed than $BaNiO_3$, but shows a flexible packing of Ba and oxygen atoms with mean Ba–O and O–O distances remarkably similar.

TABLE 3
Main Interatomic Distances (Å) and Angles (°) in $BaNi_{0.83}O_{2.5}$

Ba(1)–O(1)	2.91(5) (×2)	Ba(2)–O(3)′	3.25(4) (×2)
Ba(1)–O(1)′	2.62(6) (×2)	Ni(1)–O(1)	1.89(4) (×3)
Ba(1)–O(2)	2.83(6) (×2)	Ni(1)–O(2)	1.87(3) (×3)
Ba(1)–O(3)	2.87(4) (×2)	Ni(2)–O(1)	2.00(4) (×3)
Ba(1)–O(3)′	3.00(4) (×2)	Ni(2)–O(3)	1.91(5) (×3)
Ba(2)–O(1)	2.68(7) (×2)	Ni(3)–O(3)	2.14(5) (×6)
Ba(2)–O(1)′	2.95(9) (×2)	Ni(1)–Ni(2)	2.34(4) (×1)
Ba(2)–O(2)	2.85(2) (×2)	Ni(1)–Ni(1)	2.56(5) (×1)
Ba(2)–O(3)	2.51(5) (×2)	Ni(2)–Ni(3)	2.81(2) (×2)
O(1)–Ni(1)–O(1)	91(3) (×3)	O(1)–Ni(2)–O(3)	179(2) (×3)
O(1)–Ni(1)–O(2)	97(2) (×3)	O(1)–Ni(2)–O(3)	97(2) (×3)
O(1)–Ni(1)–O(2)	94(2) (×3)	O(3)–Ni(2)–O(3)	83(3) (×3)
O(1)–Ni(1)–O(2)	171(2) (×3)	O(3)–Ni(3)–O(3)	72(3) (×6)
O(2)–Ni(1)–O(2)	78(2) (×3)	O(3)–Ni(3)–O(3)	145(1) (×3)
O(1)–Ni(2)–O(1)	84(2) (×3)	O(3)–Ni(3)–O(3)	95(3) (×3)
O(1)–Ni(2)–O(3)	96(2) (×3)	O(3)–Ni(3)–O(3)	136(3) (×3)

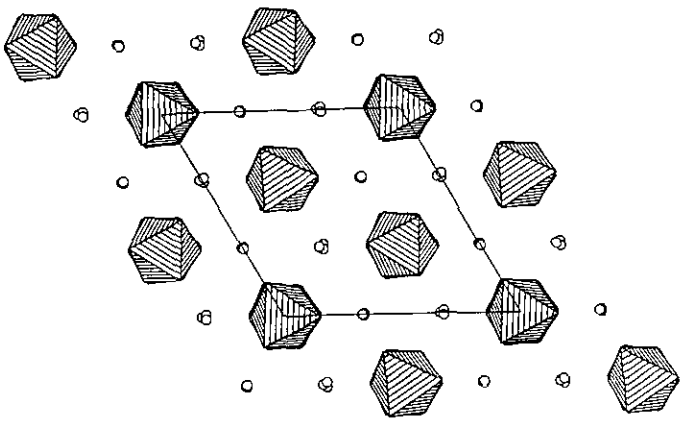

FIG. 1. Perspective of the $BaNi_{0.83}O_{2.5}$ unit-cell as seen along the **c** axis.

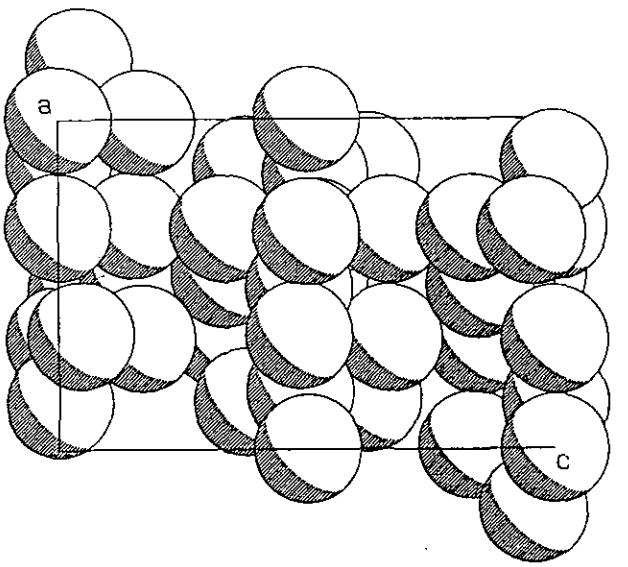

FIG. 3. Partial view of the $BaNi_{0.83}O_{2.5}$ unit-cell in which the Ba_2O_5 layers perpendicular to **c** can be distinguished.

The strong Coulomb repulsion between the highly charged Ni cations in $BaNi_{0.83}O_{2.5}$ is counterbalanced, as in $BaNiO_3$ (10), by factors like the direct overlapping of the Ni **d** orbitals, the shielding effect of the oxygens which form the opposite faces shared by the NiO_6 octahedra, and the covalent contribution present into the bonds between the small Ni ions and the oxygen atoms. The **d** orbitals overlapping is obviously much stronger for the nearest Ni(1)–Ni(2) atoms, which situate at 2.34 Å. In spite of this short distance, $BaNi_{0.83}O_{2.5}$ behaves as an electrical insulator (Fig. 4). This can be understood taking into account not only the shielding effect of the oxygens mentioned, some of them at distances smaller than those corresponding to an oxygen close packing, but also the sequence of the different Ni atoms along the chain: the shortest distances are mutually separated either by one middle distance, 2.56 Å, or by two of the longest ones, 2.81 Å. This systematic interruption of the shorter distances clearly suggest that the electrical conduction along the chain is not possible.

In contrast with $BaNiO_3$, which shows (9) a small temperature-independent paramagnetism, $BaNi_{0.83}O_{2.5}$ behaves as paramagnetic (Fig. 5) with a molar susceptibility, χ, practically constant for the magnetic field strengths employed, 50 and 5×10^4 Oe. After introducing the diamagnetic correction (14), a Curie law was obtained, χ^{-1} (cm^{-3} mole) = 6.91 T + 21.2, with a correlation factor of 0.998 for 76 increasing temperatures from 5 to 75 K, a

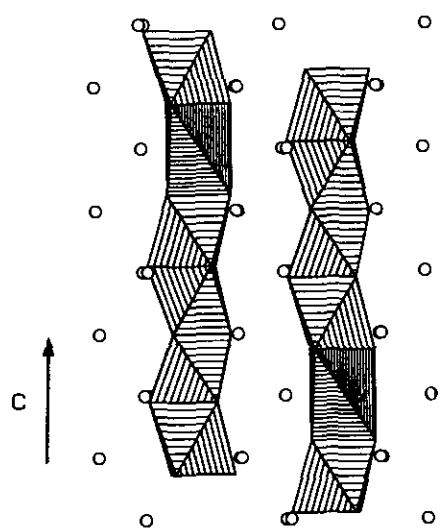

FIG. 2. Chains of NiO_6 octahedra parallel to the **c** axis in the sequence Ni(3) Ni(2) Ni(1) Ni(1) Ni(2). The darkest octahedra represent the more distorted $Ni(3)O_6$ groups.

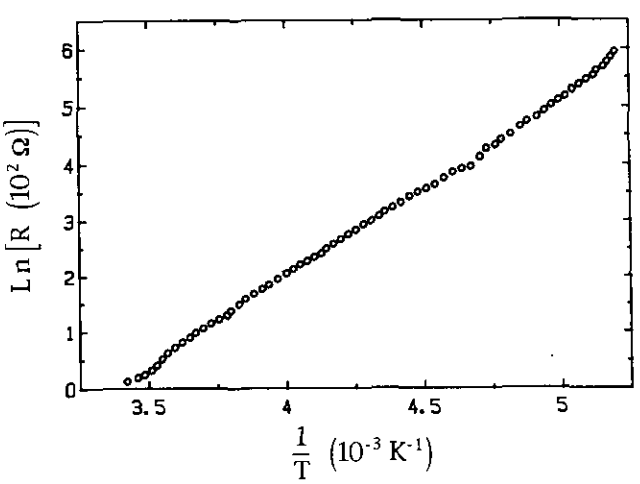

FIG. 4. Electrical resistance of $BaNi_{0.83}O_{2.5}$ vs reciprocal temperature, measured in a cylindrical bar of 3 mm^2 section and 0.5 mm length.

TABLE 4
Distances (Å) Less than 3.5 Å between Packed Ba and Oxygen Atoms in $BaNi_{0.83}O_{2.5}$

Upper layer	Same layer	Lower layer	Mean
Ba(1)–O(1) 2.91(6)	–O(2) 2.83(6) ×2	–O(1) 2.91(5)	
O(1) 2.62(4)	O(3) 2.87(7) ×2	O(1) 2.62(7)	
	O(3) 3.00(5) ×2		2.85
Ba(2)–O(2) 2.85(2)	–O(1) 2.68(7) ×2	–O(2) 2.85(5)	
O(3) 2.51(5)	O(1) 2.95(9) ×2	O(3) 2.51(8)	
O(3) 3.25(5)		O(3) 3.25(5)	2.85
O(1)–O(3) 2.92(6) ×2	–O(1) 2.69(6) ×2	–O(2) 2.81(5)	
Ba(1) 2.62(4)	O(1) 2.97(6)	O(2) 2.74(6)	
	Ba(2) 2.68(6)	Ba(1) 2.90(6)	
	Ba(2) 2.95(7)		2.81
O(2)–O(1) 2.81(8)	–Ba(1) 2.83(6) ×2	–O(1) 2.81(8)	
O(1) 2.74(7)	O(2) 2.36(6) ×2	O(1) 2.74(7)	
Ba(2) 2.85(2)	O(3) 3.36(5) ×2	Ba(2) 2.85(2)	2.83
O(3)–Ba(2) 2.51(5)	–O(2) 3.36(4)	–O(1) 2.92(6) ×2	
O(3) 3.16(5)	O(3) 2.52(10) ×2	Ba(2) 3.25(4)	
	O(3) 3.31(8)		
	Ba(1) 3.00(4)		
	Ba(1) 2.87(5)		2.94

Weiss temperature of 3.1 K and an effective magnetic moment of 1.09(3) μ_B. This can be compared with that estimated, 1.26 μ_B by the spin-only formula if one third of low spin Ni^{4+}, one third of low spin Ni^{3+}, and one sixth of Ni^{2+} per formula are assumed. This rough estimation does not take into account either the orbital contribution or another kind of subtle magnetic interactions which might exist between the Ni atoms, especially between Ni(1) and Ni(2).

According to formal ideas on chemical valence, the values found for Ni–O distances and the measured magnetic moment suggest the presence in $BaNi_{0.83}O_{2.5}$ of Ni at three different oxidation states. As the electronic structure of this oxide is not known, the alternative of oxygen 2**p** character for its holes has not to be discarded. In any case, the information provided by solving the crystal structure of the oxide here studied has allowed to establish its composition and oxygen stoichiometry as well as to correlate the kind of the atoms it contains and the atomic positions in the space with some of its physical properties.

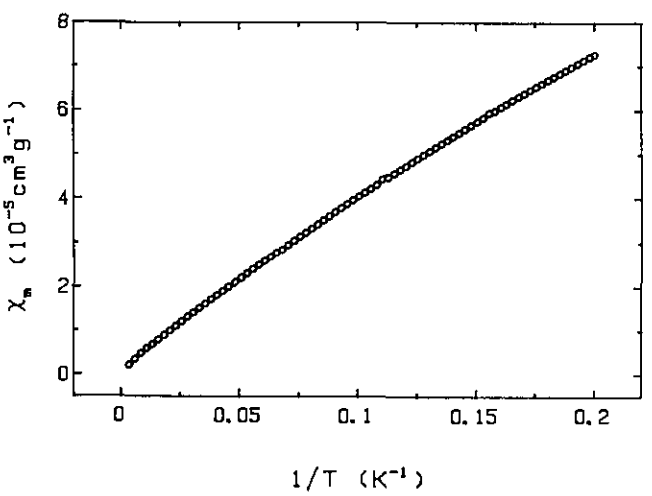

FIG. 5. Magnetic susceptibility per gram of $BaNi_{0.83}O_{2.5}$ measured at a field strength of 50 Oe, as a function of reciprocal temperature.

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