

## The Optical Properties of Lanthanides in the $Ln_2BaZnO_5$ Area of the Mixed Oxide System $Ln-Ba-Zn-O$

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The absorption spectrum of neodymium is investigated at 4.2 K in the tetragonal phase  $Ln_{4-2x}Ba_{2+2x}Zn_{2-x}O_{10-2x}$  ( $Ln = La, Nd$ ) ( $0 \leq x \leq 0.25$ ). There is evidence for a single site for which the  $4f^3$  energy levels are given. The fluorescence spectra of  $Eu^{3+}$  is analyzed in the orthorhombic phase  $Y_2BaZnO_5$ . There are two sites for the europium ions. The energy levels of  $4f^6$  are given and the crystal field parameters are determined for one of the sites. The fourth-order parameters are large. The absorption spectra of the two neodymium sites in the doped orthorhombic phases along the rare-earth series show a pronounced nephelauxetic effect (shift to the red). © 1988 Academic Press, Inc.

In their original studies of the system  $La_2O_3-BaO-CuO$ , Michel *et al.* (1, 3, 4) identified two structural families. One of them,  $La_3Ba_3Cu_6O_{14+y}$  (1), was at the onset of the recent discovery of high  $T_c$  superconductors (2). The other corresponds to the formula  $La_{4-2x}Ba_{2+2x}Cu_{2-x}O_{10-2x}$  ( $0.15 \leq x \leq 0.25$ ) (3, 4). With lanthanides beyond neodymium in the series, another phase was found with the formula  $Ln_2BaCuO_5$  (5). Copper can be replaced by zinc to give the phases  $Ln_{4-2x}Ba_{2+2x}Zn_{2-x}O_{10-2x}$  (6) and  $Ln_2BaZnO_5$  (7), structurally related to the copper compounds. The zinc phases, being white, are convenient for a study of the op-

tical properties of the lanthanides. In the present work we report the results of the measurements of the positions of the energy levels of two classical structural probes neodymium ( $4f^3$ ) and europium ( $4f^6$ ).

### Phases $Ln_{4-2x}Ba_{2+2x}Zn_{2-x}O_{10-2x}$ ( $Ln = La, Nd$ )

The phases were prepared by firing in air appropriate mixtures of  $Ln_2O_3$ ,  $BaCO_3$ , and  $ZnO$ . The mixture is ground and heated for 12 hr at  $900^\circ C$ . A further heat treatment was made at  $1000^\circ C$  for 24 hr and the product was slowly cooled back to room temperature. A single phase was obtained within the limits  $0 \leq x \leq 0.25$ .

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TABLE I  
LATTICE PARAMETERS FOR THE  $Ln_{4-2x}Ba_{2+2x}Zn_{2-x}O_{10-2x}$  ( $Ln = La, Nd$ ) PHASES  
IN THE PRESENT STUDY

	This work				Reference (6)	
	$a \pm 0.02 \text{ \AA}$	$c \pm 0.02 \text{ \AA}$	$d_{\text{obs}} \pm 0.05 \text{ g/cm}^3$	$d_{\text{cal}}$	$a$	$c$
$La_4Ba_7Zn_2O_{10}$	6.90	11.60	6.69	6.73	6.914	11.594
$La_{3.6}Ba_{2.4}Zn_{1.8}O_{9.6}$	6.90	11.60	6.66	6.62	—	—
$Nd_4Ba_7Zn_2O_{10}$	6.74	11.54	7.22	7.23	6.756	11.540
$Nd_{3.6}Ba_{2.4}Zn_{1.8}O_{9.6}$	6.74	11.54	7.00	7.09	—	—

This phase is not isomorphous to the copper compounds (for which  $0.15 \leq x \leq 0.25$  (3)). It is also a tetragonal unit cell, but the  $c$  parameter is twice the one observed for the copper compounds (6). The cell parameters that fit the X-ray powder patterns found in the present study are given in Table I with, for comparison, the values from Ref. (6). The difference with copper compounds has been attributed by Michel *et al.* (6) in their structural investigation (from X-ray powder data) to a rotation of two adjacent " $Ln_2O_3$ " structural layers. The coordination of zinc (a tetrahedron) is then different from the one for copper. To test this structural model the authors of Ref. (6) performed a powder pattern calculation in which the two heavy ions  $La^{3+}$  and  $Ba^{2+}$  were statistically distributed over the two sites 4(a) and 8(h) of the space group  $I4/mcm$ .

The absorption spectrum of the neodymium compound ( $x = 0$ ) was recorded at liquid helium temperature. It showed some traces of unreacted neodymium sesquioxide whose absorption spectrum is well known (8). Because the faint oxide absorption lines are set apart, the remaining intense absorption lines in the spectrum can be attributed to the occupation by neodymium of a single site. There is a single line for the transition from the ground state Stark level of  $^4I_{9/2}$  to  $^2P_{1/2}$  at 4 K and the number of lines observed in each  $^{2S+1}L_J$  manifold does

not exceed the number ( $J + \frac{1}{2}$ ) to be expected for the occupation of a single site of low symmetry as can be seen from the energy level sequence given in Table II. We did not try to fit this spectrum to a crystal field Hamiltonian. The values for the crystal field parameters seem to fall in a medium range. The spectrum is markedly displaced to the red (nephelauxetic effect) as expected for a material in which the oxide ion is the neodymium ligand. By comparison with known data the coordination is smaller than 9 (9). The  $^2P_{1/2}$  energy value above the ground  $^4I_{9/2}$  Stark level ( $22,930 \text{ cm}^{-1}$ ) falls between the value for  $NdOCl$  and the one for  $Nd_2O_3$ , a domain which corresponds almost exclusively up to now (see the list for 112 neodymium sites in (9)) to structures containing  $OLn_4$  tetrahedra characteristic of the lanthanide's oxysalts (built on the  $(LnO)_n^{n+}$  "complex cations" (10)). The examination of the structural model of Michel *et al.* does not show however any evidence for  $OLn_4$  tetrahedra or the classical structural layers built on their linkages.

The optical study shows the existence of a single site for the lanthanide. There is consequently no statistical distribution between barium and neodymium, and, as suspected by Michel *et al.* (6) in the discussion of their powder pattern structural data, the neodymium must occupy the "8(h)" sites with a coordination number equal to 8 and a  $C_{2v}$  site symmetry.

TABLE II  
STARK LEVEL ENERGY FOR THE  $4f^3$  CONFIGURATION AT 4.2 K IN  $\text{Nd}_4\text{Ba}_2\text{Zn}_2\text{O}_{10}$

Nominal state	$E$ ( $\text{cm}^{-1}$ )	Remarks	Nominal state	$E$ ( $\text{cm}^{-1}$ )	Remarks	
$^4I_{9/2}$	0		$^2G_{9/2}$	20,555		
	66			20,597		
	95			20,668		
	305			20,709		
	550					
$^4F_{3/2}$	11,318		$^2D(1)_{3/2}$ ,	20,849		
				20,925		
$^2H_{9/2}$ , $^4F_{5/2}$	12,233		$^4G_{11/2}$ , $^2K_{15/2}$	20,972		
	12,268			21,193		
	12,375			21,252		
	12,431			21,321		
	12,465			21,650	Large	
	12,493		$^2P_{1/2}$	22,863	Weak, $\text{Nd}_2\text{O}_3$	
12,550		22,930				
$^4S_{3/2}$ , $^4F_{7/2}$	12,623		$^2D_{3/2}$	23,443		
	13,125			23,482		
	13,212					
	13,261		$^2P_{3/2}$	25,797		
	13,313			25,880		
	13,368					
13,513		$^4D_{3/2}$	27,245			
			27,308			
$^4F_{9/2}$	14,447		$^4D_{5/2}$	27,487		
	14,598			27,616		
	14,711			27,714		
$^2H(2)_{11/2}$	15,704		$^4D_{1/2}$	28,060		
	15,789					
	15,864		$^2I_{11/2}$	28,503		
	15,886			28,514		
			28,136			
$^4G_{5/2}$	16,640		$^4D_{7/2}$ , $^2I_{13/2}$ ,	29,711		
	16,656	Weak, $\text{Nd}_2\text{O}_3$		$^2L_{15/2}$	29,953	
	16,731	Weak, $\text{Nd}_2\text{O}_3$			30,018	
	16,776			$^2D(2)_{3/2}$	32,587	
		32,780				
$^2G_{7/2}$	16,972		$^2H(1)_{11/2}$	33,616		
	17,063					
	17,195					
	17,237					
$^4G_{7/2}$	18,562					
	18,599					
	18,644					
	18,700	Weak, $\text{Nd}_2\text{O}_3$				
$^4G_{9/2}$ , $^2K_{13/2}$	18,903					
	19,058					
	19,098					
	19,172					
	19,246					
	19,269					
	19,301					
	19,605					
	19,666	Large				

TABLE III  
LATTICE PARAMETERS FOR THE ERBIUM AND THULIUM ZINC COMPOUNDS

	$a \pm 0.02 \text{ \AA}$	$b \pm 0.02 \text{ \AA}$	$c \pm 0.02 \text{ \AA}$	$d_{\text{obs}} \pm 0.05 \text{ g/cm}^3$	$d_{\text{calc}}$
$\text{Er}_2\text{BaZnO}_5$	7.03	12.26	5.68	8.47	8.42
$\text{Tm}_2\text{BaZnO}_5$	7.01	12.21	5.67	8.54	8.51

**Phases  $\text{Ln}_2\text{BaZnO}_5$  ( $\text{Ln} = \text{Sm, Eu, Gd, Dy, Ho, Er, Tm, Y}$ )**

For those heavier lanthanides and yttrium the thermal treatment was 30 hr at 1100°C. The compounds obtained have an orthorhombic unit cell and are isomorphous to the copper compounds  $\text{Ln}_2\text{BaCuO}_5$  (5). The cell parameters derived from the powder pattern data for the Er and Tm zinc compounds were not previously reported in the literature and are given in Table III. The Er and Tm compounds were fired at a slightly higher temperature (1150°C) and for a longer time (36 hr).

The structure was established (on powder patterns) by Michel and Raveau (7) and shows two sites for the lanthanide (or yttrium) in the 4(c) positions of the space group  $Pbnm$ . The coordination number for the two sites is 7, according to the determination of the light atoms positions. The site symmetry is  $C_s$ .

The fluorescence spectrum of  $\text{Eu}^{3+}$  doping the yttrium phase shows, for the transitions from the upper fluorescent level  $^5D_0$  to the ground  $^7F_J$  manifold, two systems of lines corresponding to the occupation of two europium sites in the structure. The fluorescence of each of the two sites was selectively excited with a Rhodamine 6G dye laser, and from these experiments, the sequence of energy levels for the  $4f^6$  configuration was obtained. The results are given in Table IV; the experimental spectra are shown in Fig. 1. The pure Europium compound yielded absorptions corresponding to the components of  $^5D_1$  and  $^5D_2$  (Fig. 2).

One of the sites (labeled "site II") is almost axial because two of the three lines in the  $^5D_0 \rightarrow ^7F_1$  transition are very close (see the splitting of the  $^7F_1$  level in Fig. 1). The spectrum for this site was fitted with standard methods, of the type described in de-

TABLE IV  
EXPERIMENTAL ENERGY LEVELS FOR THE TWO EUROPIUM SITES IN  $\text{Y}_2\text{BaZnO}_5$  AT 77 K FROM THE ANALYSIS OF THE FLUORESCENCE SPECTRA

Nominal state	$E \text{ (cm}^{-1}\text{)}$ site I	$E \text{ (cm}^{-1}\text{)}$ site II
$^7F_0$	0	0
$^7F_1$	338	314
	349	363
	357	371
	865	884
$^7F_2$	927	941
	1,202?	1,186?
	1,225?	1,198?
	1,244?	1,215?
$^7F_3$	1,841	1,837
	1,870	1,882
	1,890	1,893
	1,925	1,938
	1,941	1,981
	1,953	
	1,978	
$^7F_4$	2,565	2,599
	2,726	2,697
	2,826	2,824
	2,936	2,940
	3,005	2,956
	3,022	2,988
$^5D_0$	3,094	3,047
	3,107	3,060
	17,157	3,116
		17,139

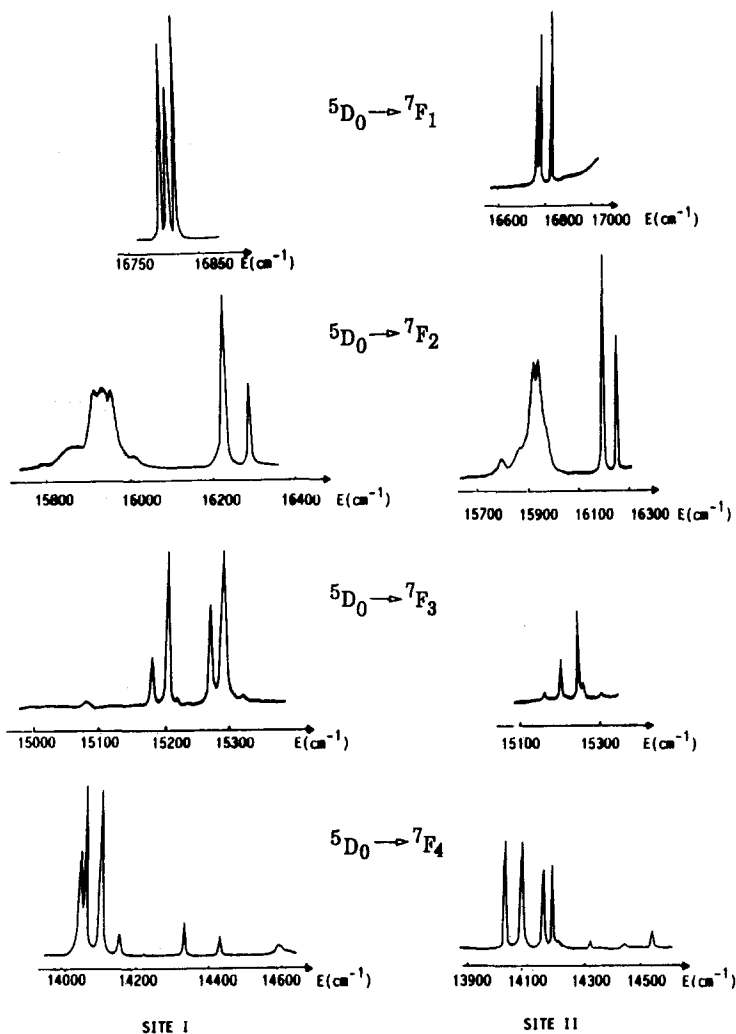


FIG. 1. Experimental fluorescence spectra for "site I" (dye-laser excitation at  $17,157 \text{ cm}^{-1}$ ) and for "site II" (dye-laser excitation at  $17,139 \text{ cm}^{-1}$ ) in  $\text{Eu}^{3+}$  (1%):  $\text{Y}_2\text{BaZnO}_5$ ;  $T = 77 \text{ K}$ .

tail in Ref. (11), to a  $C_{2v}$  Hamiltonian (an approximation for the true  $C_s$  symmetry), with the procedure of descending symmetry, assuming first a  $C_{4v}$  dominant crystal field as suggested by a point charge electrostatic calculation of a first set of approximate crystal field parameters done through standard lattice sum computations using the structural data reported in (7). A convenient fit was found especially when the three highest " ${}^7F_2$ " levels reported in Table

IV were taken out of the fitting procedure. Those levels may be associated to vibronic lines quite common on the "red" side of the  ${}^5D_0$  to  ${}^7F_2$  transition. The result of the fitting is given in Table V. The crystal field parameters obtained (Table VI) are defined with respect to the  $c$  axis in the structure described in (7) and are characterized by large values of the fourth-rank parameters, small second-rank parameters, and medium sixth-order parameters. This is a very com-

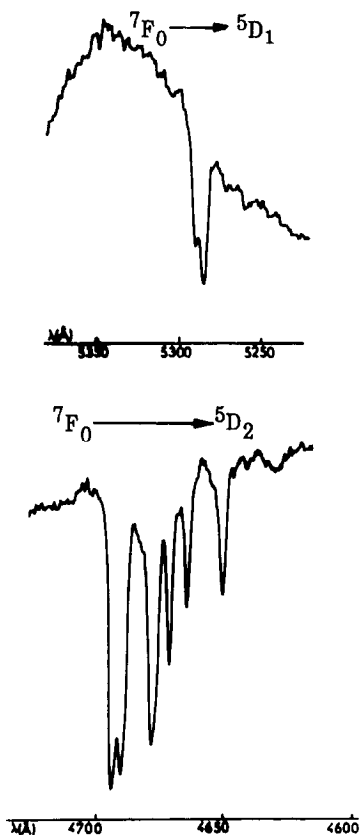


FIG. 2. Absorption spectra for  $\text{Eu}_2\text{BaZnO}_5$ ;  $T = 10$  K.

mon situation for compounds in which the oxide ion is the ligand. The crystal field parameters are then dominated by the fourth order's  $B_q^k$  (see examples in (9)). Those parameters are sensitive to contributions from covalent effects in the chemical bond (12–14). The crystal field parameters for the less symmetric "site I" were not determined but the examination of Table IV shows that they are not very different from those of "site II."

We also doped some of the phases with neodymium and recorded the absorption spectra at liquid helium temperature. Two sites are seen from the two components of the transition from the ground state to  ${}^2P_{1/2}$  (Fig. 3). The energy positions versus the

TABLE V  
FITTING OF THE EXPERIMENTAL ENERGY LEVELS OF THE EUROPIUM ION IN "SITE II" AT 77 K TO A  $C_{2v}$  CRYSTAL FIELD HAMILTONIAN WITH THE PARAMETERS IN TABLE VI

Nominal state	$E_{\text{exp.}}$ (cm $^{-1}$ )	$E_{\text{calc.}}$ (cm $^{-1}$ )	Irreducible representation
${}^7F_0$	0	0	A1
${}^7F_1$	314	314	A1
	363	362	A2
	371	371	B1
${}^7F_2$	884	884	A1
	941	941	A1
	—	1064	B1
	—	1147	A2
	—	1149	B2
${}^7F_3$	—	1773	A1
	1837	1847	B2
	1882	1865	A2
	1893	1894	B1
	1938	1934	A2
	—	1962	B2
	1981	1992	B1
${}^7F_4$	2599	2601	A2
	2697	2698	B2
	2824	2819	B1
	2940	2932	A1
	2956	2958	A1
	2988	3006	A2
	3047	3044	B1
	3060	3062	B2
$\sigma$	3116	3109	B1
		9	

ionic radii of the rare earths are given in Fig. 4. The data for the tetragonal lanthanum and neodymium compounds single site fall almost on line with the data for one

TABLE VI  
 $C_{2v}$  CRYSTAL FIELD PARAMETER VALUES FOR THE EUROPIUM ION IN "SITE II"

$B_q^k$ (cm $^{-1}$ )	Fitting on 19 levels
$B_0^2$	$72.3 \pm 19.8$
$B_2^2$	$75.8 \pm 11.5$
$B_0^4$	$1496.0 \pm 48.1$
$B_2^4$	$-197.7 \pm 52.2$
$B_4^4$	$1300.0 \pm 35.9$
$B_0^6$	$-569.7 \pm 34.4$
$B_2^6$	$431.1 \pm 44.2$
$B_4^6$	$-283.9 \pm 29.4$
$B_6^6$	$-9.7 \pm 41.7$

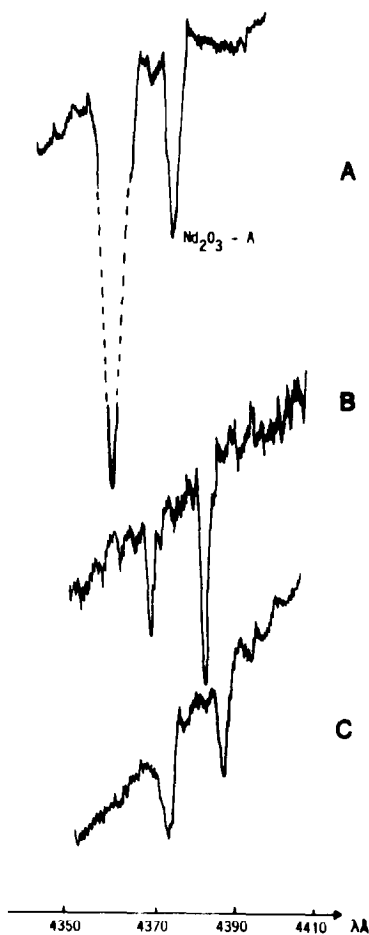


FIG. 3. Absorption spectra at  $T = 4.2$  K for Nd in  $A = \text{Nd}_4\text{Ba}_2\text{Zn}_2\text{O}_{10}$ ,  $B = \text{Nd (10\%): Gd}_2\text{BaZnO}_5$ ,  $C = \text{Nd (10\%): Er}_2\text{BaZnO}_5$ .

of the sites of the orthorhombic structure. This indicates some basic structural relationship between the two structures. In fact the examination of the figures showing the lanthanide's coordination polyhedra, Fig. 1 in (6) and Fig. 2 in (5), shows a close similarity of the lanthanide's oxygen ligand geometry in the two structures. In the case of the lanthanum zinc compound (6), there are four oxygens at 2.74 Å, two at 2.55 Å, and two at 2.32 Å (mean 2.59 Å); for the yttrium zinc compound the sets of distances are for the site labeled Y(1) in (7) with two oxy-

gens at 2.20 Å, three at 2.34 Å, and two at 2.48 Å (mean 2.34 Å); and for the site labeled Y(2) there are three oxygens at 2.30 Å, two at 2.35 Å, and two at 2.49 Å (mean 2.37 Å). For the same dopant (neodymium) the mean distance will be larger in the case of the lanthanum compound; however, the differences in term of mean distances are not very significant between the two sites in the yttrium compound, but two oxygen atoms are closer for the site labeled Y(1). Nevertheless the two sites are clearly distinguished by their nephelauxetic position as shown in Fig. 4.

The data for the lowest line in Fig. 4 are in fact the lowest nephelauxetic positions recorded for a neodymium site in a structure (9). It may correspond to the occupation by neodymium of the site Y(1). It is impossible, however, to make any correlation with the results of the europium study because it is difficult to compare the neodymium and the europium nephelauxetic scales (9).

Neodymium is a very good probe for the determination of the variations of the free-atom parameters of the  $4f^N$  configurations with structure. A quantitative relationship cannot however be yet established (9). There is no correlation with crystal field parameters values. The only empirical correlation which can be established, and which is perfectly evident from Fig. 4, is with the shortening of the "distance" to the ligand illustrated here by the lanthanide's contraction. However, a recent calculation (15) shows that the nephelauxetic effect is indeed linked to the covalent overlap of the lanthanide's wave functions with the ligand orbitals. It can be translated as the indication of a "stress" (or a "pressure") applied on the lanthanide. There is consequently from our optical data a rough indication that the lanthanide in those complex oxides is submitted to some kind of unusual "internal pressure" from the overall structural arrangement.

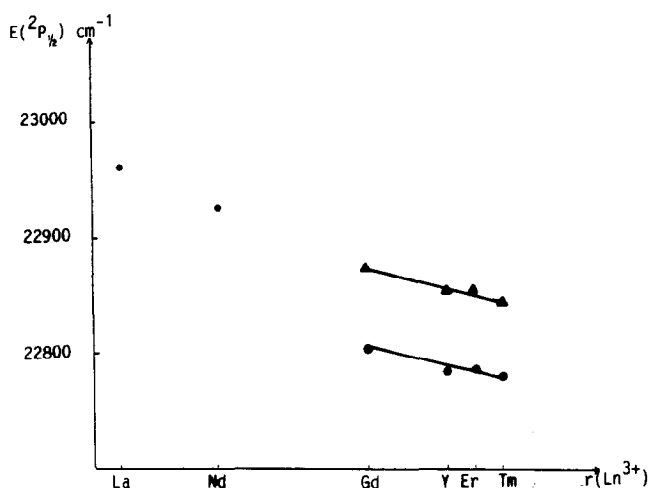


FIG. 4. Positions of the  $^2P_{1/2}$  levels of  $4f^3$  at 4.2 K versus the ionic radii of the rare earths in the phases investigated.

The rather complex absorption spectrum (because of the two sites) of the erbium compound was also recorded at liquid helium temperature.

In the course of this study the copper compounds  $Y_{2-x}Ba_{1+x}CuO_{5-y}$  for  $x = 0.2$  and  $x = 1$  and  $La_{2-x}Ba_{1+x}CuO_{5-y}$  for  $x = 0$  and  $x = 0.2$  were investigated for superconductivity. The method of preparation was the same as that described in Ref. (16). No superconductivity was found in agreement with the results in (16), but the lanthanum compounds showed a large paramagnetic effect below 5 K due presumably to some kind of magnetic ordering (17).

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