

Journal of Alloys and Compounds 241 (1996) 82-88

ALLOYS AND COMPOUNDS

# Structure-property relationships in a series of mixed layer pnictide oxide compounds: $A_2Mn_3Pn_2O_2$ (A = Sr, Ba; Pn = P, As, Sb)<sup>1</sup>

Stephanie L. Brock, Susan M. Kauzlarich\*

Department of Chemistry, University of California, Davis, CA 95616, USA

Received 11 March 1996

#### Abstract

Results of magnetic property measurements for the compounds  $A_2Mn_3Pn_2O_2$  (A = Sr, Ba; Pn = P, As, Sb) are reported and discussed in the light of structural trends in the series. The structure consists of a 1:1 intergrowth of metal oxide layers in which the metal coordination is square planar and metal pnictide layers in which the coordination is tetrahedral. With the exception of  $Sr_2Mn_3As_2O_2$ , magnetic susceptibility data reveal the presence of broad maxima that have been assigned to coupling of the  $MnO_2^{2-}$  layers. The data have been fitted assuming a 2D Heisenberg antiferromagnet model and the intraplanar coupling constants obtained are observed to increase as the *a* parameter or metal oxygen bond length decreases. The same trend is observed for the relationship of transition temperatures, obtained from  $d_X T/dT$  plots, to the *a* axial parameters. The exception to the rule is  $Sr_2Mn_3As_2O_2$ , which has an anomalously low transition temperature and different magnetic behavior for field-cooled versus zero-field-cooled samples. The field-cooled data show a sharp antiferromagnetic transition whereas the zero-field-cooled data show no transition to 3D order between 5 and 300 K.

Keywords: 2D magnetism; Antiferromagnetism; Semiconductivity; Layered compounds; Pnictide oxide compounds

# **1. Introduction**

Layered transition metal oxides and pnictides have been well studied. Interest in these compounds stems from properties which are associated with both the chemical components and the specific layered structure, such as superconductivity, charge density waves, and low-dimensional magnetism [1]. At the intersection of these two classes of compounds is the small group of layered transition metal pnictide oxide compounds [2-9]. In contrast to pnictate or pnictite compounds (e.g. arsenate, phosphite), in the pnictide oxides both pnictogen and oxygen are anions and there is no bonding between them. We have been investigating a series of compounds of the Sr<sub>2</sub>Mn<sub>3</sub>As<sub>2</sub>O<sub>2</sub> tetragonal structure type [3,6,9]. They are designated as mixed layer compounds because they have independent metal pnictide and metal oxide layers, and the structure is shown in Fig. 1. Two requirements for the formation of this structure type

A2Mn3Pn2O2 (A=Sr,Ba, Pn=P,As,Sb,Bi)



Fig. 1. A view of the unit cell of the mixed layer transition metal pnictide oxides of the  $Sr_2Mn_3As_2O_2$  structure type and a list of the known manganese containing compounds which crystallize in this structure type.

<sup>\*</sup> Corresponding author.

<sup>&</sup>lt;sup>1</sup> Dedicated to Professor Dr. Dr. h.c. Hans Georg von Schnering on his 65th birthday.

83

are lattice matching and chemical compatibility of the two layers. The effect of changing the alkaline earth cation and the pnictogen is to move the layers further apart or closer together. The identity of the alkaline earth and the pnictogen also influences the intraplanar bond distances. It is possible to probe these structural effects on the nature of the bonding through property measurements. A neutron diffraction study performed on Sr<sub>2</sub>Mn<sub>3</sub>As<sub>2</sub>O<sub>2</sub> and Sr<sub>2</sub>Mn<sub>3</sub>Sb<sub>2</sub>O<sub>2</sub> has revealed the presence of two different magnetic lattices due to independent coupling of the metal oxide and metal pnictide layers [10]. This paper describes magnetic property measurements for A<sub>2</sub>Mn<sub>3</sub>Pn<sub>2</sub>O<sub>2</sub> (A = Sr, Ba; Pn = P, As, Sb) and discusses them in the light of the neutron study and the bonding in these compounds.

# 2. Experimental procedures

## 2.1. Materials

AO (A = Sr, Ba) was prepared from thermal decomposition of ACO<sub>3</sub> (Johnson Matthey, 99.999%) under vacuum (1000°C, 48 h). Mn flake (Johnson Matthey, 99.9%) was etched with 15% by volume HNO<sub>3</sub> in methanol and rinsed with acetone before use. P (Johnson Matthey, 99.999%), As and Sb (Johnson Matthey, 99.9999%) were used as received without further purification. All materials were handled in a drybox under argon and ground, using a mortar and pestle, before use.

### 2.2. Synthesis

A stoichiometric mixture of AO (A = Sr, Ba), Mn, and Pn (Pn = P, As, Sb) was ground together in a mortar and pestle in an N<sub>2</sub>-filled drybox and pressed into a pellet (5000 psi). The pellets were then placed in an alumina boat and sealed in a fused silica ampoule under 0.5 atm of argon. The samples were heated to 1000°C at a rate of 30°C h<sup>-1</sup>, left for one week, and rapidly cooled. With the exception of  $Ba_2Mn_3P_2O_2$ , which decomposes over a period of a few days, no decomposition of the products was observed over weeks in air.

## 2.3. X-ray powder diffraction

The products were ground with a mortar and pestle, mixed with silicon and placed between two pieces of cellophane tape so they could be characterized via X-ray powder diffraction. Powder patterns were obtained using an Enraf-Nonius Guinier camera utilizing Cu K $\alpha_1$  radiation. The results were compared with patterns calculated from crystal structure data using the program POWDER [11] in order to assess purity. All the samples used in the measurements reported herein showed no other phases aside from the desired product. Lattice parameters were obtained by standard least-squares refinement and are provided in Table 1. They are in good agreement with published single crystal results [3].

## 2.4. magnetic susceptibility measurements

A Quantum Design SQUID magnetometer was employed for magnetic measurements. Magnetic data were collected on powder samples sealed in a fused silica tube, designed to provide negligible background, under vacuum. Magnetization versus field data were taken at 5 K over the range  $100-10\,000$  G, and magnetization versus temperature data were obtained from 5-300 K in a field of 2 or 5 kG. Field-cooled (FC) and zero-field-cooled (ZFC) magnetization versus temperature data were collected.

# 3. Results and discussion

The first synthesis reported by Brechtel, Cordier and Schäfer [3] in 1979 for the compounds  $A_2Mn_3Pn_2O_2$  involves heating A, Mn, Pn, and  $Pn_2O_3$ to 1250-1400°C (A = Sr, Ba; Pn = As, Sb, Bi). Under these conditions, crystals suitable for X-ray structure determinations are produced, however, the products are reported to be mixed phase. In 1991, Stetson and

Table 1

Summary of magnetic and crystallographic data for the compound	ds $A_2Mn_2Pn_2O_2$ (A = Sr, Ba; Pn = P, As, Sb)	

Compound	<i>Τ<sub>χ max</sub></i> (K)	<i>Т</i> <sub>N</sub> (К)	$\frac{J}{k_B}(\mathbf{K})^{\mathbf{b}}$	a (Å)	c (Å)
Sr <sub>2</sub> Mn <sub>3</sub> As <sub>2</sub> O <sub>2</sub>	$51(2)[T_1]$ $65(2)[T_1]$	46(2)*	N/A	4.1459(6)	18.856(2)
Ba,Mn,P.O.	125(5)	98(7)	12.7(2)	4.2029(7)	19.406(5)
Ba, Mn, As, Ó,	100(7)	74(5)	10.2(2)	4.2539(5)	19.755(4)
Sr,Mn,Sb,O,	79(2)	62(2)	7.45(8)	4.2599(4)	20.093(3)
Ba, Mn, Sb <sub>2</sub> O,	69(2)	44(2)	6.67(7)	4.3650(2)	20.789(2)

<sup>a</sup>  $T_{\rm N}$  is ascribed to the more pronounced magnetic transition,  $T_{\rm 1} = 51(2)$  K.

<sup>b</sup> The 2D Heisenberg model has not been applied to Sr<sub>2</sub>Mn<sub>3</sub>As<sub>2</sub>O<sub>2</sub>.

Kauzlarich [9] reported a new synthesis employing AO, Mn, and Pn as starting materials, and heating to 1000°C for one week. A new pnictide oxide,  $Ba_2Mn_3P_2O_2$ , was produced by this method and characterized via X-ray powder diffraction. This synthesis is also successful in producing pure microcrystalline samples of the barium analogs  $Ba_2Mn_3Pn_2O_2$  (Pn = As, Sb).  $Sr_2Mn_3P_2O_2$  apparently cannot be prepared by either method, but the As and Sb compounds can be prepared in quantitative yields (at least 95% based on Guinier X-ray powder diffraction) by employing SrO, Mn, and the appropriate pnictogen element. To date, it has not been possible to produce  $Sr_2Mn_3Bi_2O_2$ in high yield by this synthetic route. All materials are obtained as grey-black powders. The compounds  $A_2Mn_3Pn_2O_2$  (A = Sr, Ba; Pn = P, As, Sb) all crystallize in the tetragonal space group 14/mmm [3]. Selected bond distances are listed in Table 2 [3,9]. The structure consists of a 1:1 intergrowth of  $Mn_2Pn_2^2$ and  $MnO_2^{2-}$  layers separated by the alkaline earth cations. The  $Mn_2Pn_2^{2-}$  layers are isostructural to those in the ThCr<sub>2</sub>Si<sub>2</sub> (or BaAl<sub>4</sub>) structure type [12] consisting of an Mn square planar network alternatively capped above and below the plane by pnictogen atoms to form an edge-shared  $MnPn_{4/4}^{1-}$  tetrahedral network. The  $MnO_2^{2-}$  layers contain Mn in a square planar environment of oxygen atoms, isostructural to CuO<sub>2</sub> planes in high  $T_c$  superconductors. The structure is composed such that the Pn atoms from the  $Mn_2Pn_2^{2-}$ layers point directly towards the Mn atoms of the  $MnO_2^{2-}$  layers, creating a pseudo-octahedral environment. The Mn-Pn interplanar distance, however, is considerably longer than a bond. These distances are roughly 0.6–0.9 Å longer than the corresponding intraplanar distances and are on the order of a van der Waals interaction [13]. As can be seen from Table 2, the interplanar Mn-Pn distance varies significantly with the size of the alkaline earth cation and the pnictogen anion.

## 3.1. Magnetism

All samples, with the exception of  $Sr_2Mn_3As_2O_2$ and  $Sr_2Mn_3Sb_2O_2$ , were magnetically pure and showed linear dependence of magnetization measurements as a function of field at 5 K from 0-1 T. Sr<sub>2</sub>Mn<sub>3</sub>As<sub>2</sub>O<sub>2</sub> and Sr<sub>2</sub>Mn<sub>3</sub>Sb<sub>2</sub>O<sub>2</sub> have a ferromagnetic contribution to the magnetism, attributed to the binary impurities MnAs or MnSb. This is indicated by a slight turn-over of the magnetization with increasing field, as shown in Fig. 2. Successive annealing of the samples three times with 10% excess SrO was not successful in removing all of the ferromagnetic impurities, although the amount of deviation from linearity could be minimized. These ferromagnetic impurities cannot be detected from X-ray diffraction, suggesting that they are present as less than 5% of the sample. The impurities have  $T_{\rm c}$  values above room temperature and we suspect that they might be MnAs  $(T_c = 317 \text{ K})$  [14] and MnSb  $(T_c = 556 \text{ K})$  [15]. There is a clear signature of a ferromagnetic transition above 300 for the  $Sr_2Mn_3As_2O_2$ , consistent with the presence of MnAs. The fraction of impurity could be calculated from the magnetization versus field data for  $Sr_2Mn_3As_2O_2$  and  $Sr_2Mn_3Sb_2O_2$ . If the ferromagnetic impurities are assumed to be MnAs and MnSb respectively, there is an estimated 5% MnAs in the  $Sr_2Mn_3As_2O_2$  sample by molar volume and 2% of MnSb in the  $Sr_2Mn_3Sb_2O_2$  sample.

Magnetic susceptibility measurements as a function of temperature for all the compounds except



Fig. 2. Magnetization as a function of field for the compounds Sr<sub>2</sub>Mn<sub>3</sub>Sb<sub>2</sub>O<sub>2</sub> and Sr<sub>2</sub>Mn<sub>3</sub>As<sub>2</sub>O<sub>2</sub>.

Selected bond distances (A) in the compounds $A_2Mn_3Pn_2O_2$ (A = Sr; Ba; Pn = P, As, Sb) <sup>-</sup>							
Compound	Mn(2)-Mn(2)	Mn(2)-Pn	Mn(1)-Pn <sup>c</sup>	Mn(1)-O	A-Pn	A-0	
Sr <sub>2</sub> Mn <sub>3</sub> As <sub>2</sub> O <sub>2</sub>	2.939(12)	2.574(1)	3.191(2)	2.078(1)	3.340(3)	2.625(2)	
Ba <sub>2</sub> Mn <sub>3</sub> P <sub>2</sub> O <sub>2</sub> <sup>h</sup>	2.972(7)			2.101(1)			
Ba, Mn, As, O <sub>2</sub>	3.004(7)	2.593(1)	3.458(4)	2.124(1)	' 3.457(3)	2.748(2)	
Sr <sub>2</sub> Mn <sub>3</sub> Sb <sub>2</sub> O <sub>2</sub>	3.014(5)	2.741(1)	3.304(3)	2.131(1)	3.471(4)	2.654(2)	
Ba <sub>2</sub> Mn <sub>3</sub> Sb <sub>2</sub> O <sub>2</sub>	3.088(7)	2.755(2)	3.516(2)	2.183(1)	3.578(3)	2.772(3)	

Table 2

\* From Refs. [3,9].

<sup>b</sup> A single crystal structure determination was not performed. Bond distances for atoms on special positions that have no variable components have been calculated from the known lattice parameters.

<sup>c</sup> Calculated using the lattice parameters and atomic coordinates provided in Ref. [3].



Fig. 3. Magnetic susceptibility as a function of temperature for the compounds  $Ba_2Mn_3Pn_2O_2$  (Pn = P, As, Sb) and  $Sr_2Mn_3Sb_2O_2$ .

 $Sr_2Mn_3As_2O_2$ , which is discussed below, are presented in Fig. 3 and the data are summarized in Table 1. All compounds show a broad maximum indicative of low dimensional antiferromagnetic coupling [16]. A determination of the transition temperatures can be obtained from measurements of the magnetic contribution,  $d\chi T/dT$ , which is proportional to the heat capacity [17]. The Néel temperatures, which are obtained from the maxima in these first derivative plots, are presented in Table 1.

Interpretation of the susceptibility data for this series of compounds has been simplified by a neutron diffraction study of two members of the series:  $Sr_2Mn_3As_2O_2$  and  $Sr_2Mn_3Sb_2O_2$  [10]. In brief, the neutron data indicate the presence of two different magnetic lattices in these materials, one which orders near room temperature and one which orders at low temperature (50-100 K). The room temperature magnetic lattice can be modeled as antiferromagnetic coupling both within and between the  $Mn_2Pn_2^{2-}$  layers and is the same in both compounds. The low temperature magnetic lattice can be ascribed to coupling of the  $MnO_2^{2-}$  layers, but the details are different for the two compounds. For Sr<sub>2</sub>Mn<sub>3</sub>Sb<sub>2</sub>O<sub>2</sub> the magnetic lattice is identical to that of K<sub>2</sub>NiF<sub>4</sub> [18], consisting of antiferromagnetic intraplanar interactions and ferromagnetic interactions between next nearest  $MnO_2^{2-}$  layers along c. In contrast, for Sr<sub>2</sub>Mn<sub>3</sub>As<sub>2</sub>O<sub>2</sub> the magnetic reflections corresponding to the  $MnO_2^{2-}$  sublattice are very weak and the most prominent reflection has a Warren line shape [19] indicative of short range order.

The neutron powder diffraction study on  $Sr_2Mn_3Sb_2O_2$  is consistent with 2D antiferromagnetic coupling of the  $Mn_2Pn_2^{2-}$  layers at temperatures above 300 K and 2D antiferromagnetic coupling of the  $MnO_2^{2-}$  layers below 300 K. This 2D coupling arises from the layered nature of the compounds and is reinforced by the geometry of the metal oxide sublattice. The  $MnO_2^{2-}$  sublattice is composed of square



Fig. 4. Illustration of the stacking of the  $Mn_2Pn_2^{2-}$  and  $MnO_2^{2-}$  sublattices along *c* and the magnetic model for coupling in  $Sr_2Mn_3Sb_2O_2$ . The circles represent Mn atoms and the shading indicates the spin direction. (a) The  $Mn_2Pn_2^{2-}$  layers are coupled antiferromagnetically both within and between the layers. (b) The  $MnO_2^{2-}$  layers are coupled antiferromagnetically to the next nearest neighboring layer. Interactions between nearest neighboring layers cancel due to symmetry mismatch.

 $MnO_{4/2}^{2-}$  units which are shifted relative to each other by 1/2 along the *ab* diagonal, then stacked along *c* (Fig. 4). This stacking mode precludes simple antiferromagnetic coupling in both the *ab* plane and to the nearest  $MnO_2^{2-}$  layer along *c* and the interactions cancel. Therefore 3D ordering occurs via interactions between next nearest  $MnO_2^{2-}$  layers over a distance of approximately 20 Å. The same sort of lattice mismatch is perpetually present between the metal oxide and metal pnictide layers and results in no net interaction between the two sublattices (i.e. they couple independently) [10].

The magnetic susceptibility versus temperature data for  $\text{Sr}_2\text{Mn}_3\text{Sb}_2\text{O}_2$  and the three Ba compounds  $\text{Ba}_2\text{Mn}_3\text{Pn}_2\text{O}_2$  (Pn = P, As, Sb) were all very similar. This suggests that the magnetic structure deduced from neutron powder diffraction for  $\text{Sr}_2\text{Mn}_3\text{Sb}_2\text{O}_2$  is applicable to the Ba compounds as well. The  $T_N$ (obtained from the  $d\chi T/dT$  plot) for  $\text{Sr}_2\text{Mn}_3\text{Sb}_2\text{O}_2$  is at 62 K, which is consistent with the value of 65 K obtained by neutron diffraction for the coupling of the  $\text{MnO}_2^{2^-}$  layers. Thus, the magnetic susceptibility data (300–5 K) probes the metal oxide sublattice independently and a straightforward analysis of the susceptibility is therefore possible.

The cell dimensions a and c expand and contract together as the alkaline earth cation and the pnictogen anion are substituted across the series. This changes the nature of the intraplanar bonding as well as the interaction between the layers. Because of the long interplanar coupling distances, the intraplanar coupling constant is expected to be several orders of magnitude greater than the interplanar coupling constant [20]. Indeed, the 3D coupling of the metal oxide sublattice can be viewed as a secondary effect, arising when the correlation length for coupling within the layers becomes sufficiently long to induce coupling between the layers [21]. Intraplanar coupling constants have been obtained by a least-squares fitting of the inverse susceptibility data to a 2D Heisenberg model, as illustrated in Fig. 5 and Table 1 [20].

The intraplanar exchange constants can be directly related to the a parameters and the Mn–O bond distances, as illustrated in Fig. 6. As the a lattice parameters decrease, the coupling constants increase. This suggests that the coupling within the layer is facilitated by stronger Mn–O bonding, consistent with



Fig. 5. Fit of the inverse susceptibility data for (a)  $Ba_2Mn_1P_2O_2$ , (b)  $Ba_2Mn_1As_2O_2$ , (c)  $Sr_2Mn_3Sb_2O_2$ , and (d)  $Ba_2Mn_3Sb_2O_2$  to a 2D Heisenberg antiferromagnet model.



Fig. 6. Plot of  $J/k_{\rm B}$  as a function of the *a* axial parameter and the Mn-O bond distance. The line indicates the trend of the data.

a coupling mechanism of superexchange through oxygen [22]. As illustrated in the plot of transition temperature as a function of *a* axial parameter presented in Fig. 7, the behavior of the transition temperatures follows the same trend as the exchange constants. The well-behaved nature of these trends is an indication that these compounds all have similar electronic structures and the transition temperature is chiefly determined by the distance between the spins. The only exception is  $Sr_2Mn_3As_2O_2$ , which has an anomalously low transition temperature. This is a strong indication that the coupling in this compound is of a different nature.

 $Sr_2Mn_3As_2O_2$  demonstrates unique magnetic behavior. All other compounds show identical FC and ZFC temperature dependent magnetic susceptibility



Fig. 7. Plot of the transition temperatures  $T_c$  as a function of the *a* axial parameter. The line indicates the trend in the data.



Fig. 8. FC and ZFC magnetic susceptibility as a function of temperature for  $Sr_2Mn_3As_2O_2$ .

behavior. FC and ZFC temperature dependent magnetic susceptibility data are shown in Fig. 8 for Sr<sub>2</sub>Mn<sub>3</sub>As<sub>2</sub>O<sub>2</sub>. The FC magnetic susceptibility data show a sharp maxima near 50 K, reminiscent of a 3D antiferromagnet, whereas the ZFC data show a broad. poorly defined transition below 50 K. This behavior is opposite to that which is expected for a spin-glass The overall system [23]. susceptibility for  $Sr_{2}Mn_{3}As_{2}O_{2}$  is approximately five times larger than for the other members of the series. Additionally, there is a pronounced knee on the high temperature end of the maximum in the susceptibility of the fieldcooled sample.  $T_1$  and  $T_2$  are indicated in Fig. 8 and correspond to the maximum, and a knee, in the susceptibility at 51 and 65 K respectively. The Néel temperature, calculated by plotting  $d\chi T/dT$  for  $Sr_2Mn_3As_2O_2$ , is 46(2) K and is presumed to correlate with  $T_1$  (51 K). The fact that the transition temperature is close to the maximum in the susceptibility is suggestive of 3D antiferromagnetic coupling in this compound when field-cooled [17].

Unique behavior for  $Sr_2Mn_3As_2O_2$  is also noted in the neutron diffraction data [10]. Neutron diffraction measurements indicate short range order commencing at about 75 K and persisting down to 4 K for the  $MnO_2^{2-}$  sublattice. This is consistent with the ZFC magnetic susceptibility data which show a broad maximum indicating no transition to an ordered state down to 5 K. One possible explanation for this behavior is that structural changes are resulting in radically different behavior in Sr<sub>2</sub>Mn<sub>3</sub>As<sub>2</sub>O<sub>2</sub>. Sr<sub>2</sub>Mn<sub>3</sub>As<sub>2</sub>O<sub>2</sub> has the smallest c parameter of any compound of the series and the closest Mn-Pn interlayer distance. The unusual dependence on FC versus ZFC and the apparent presence of two features  $(T_1 \text{ and } T_2)$  in the magnetic susceptibility indicate that this coupling may be quite complex. Further magnetic studies and neutron diffraction studies varying magnetic field and time parameters are necessary to probe this order more thoroughly.

# 4. Conclusions

This paper presents the first systematic study of structure-property relationships in the layered pnictide oxides of the  $Sr_2Mn_3As_2O_2$  structure type. The  $Mn_2Pn_2^{2-}$  lattice orders antiferromagnetically above 300 K and only one transition is observed in temperature dependent susceptibility measurements which is attributed to the  $MnO_2^{2-}$  sublattice. This model is supported by neutron powder diffraction data for  $Sr_2Mn_3Sb_2O_2$  [10]. The coupling is antiferromagnetic and strongly two-dimensional in nature, consistent with the layered nature of the materials. Intraplanar coupling constants have been obtained by fitting the susceptibility data to a 2D Heisenberg model and coupling increases as the metal oxygen bond length decreases. Transition temperatures for the series are also observed to increase as a decreases, further emphasizing the relationship between distance and strength of coupling. The exception is  $Sr_2Mn_3As_2O_2$ which has the smallest cell and yet an anomalously low transition temperature. The behavior of the magnetic susceptibility of Sr<sub>2</sub>Mn<sub>3</sub>As<sub>2</sub>O<sub>2</sub> is unique and further measurements are necessary to gain a better understanding of the magnetic interactions in this compound.

## Acknowledgements

We thank Ned Stetson for his contribution to the early part of this work, and Robert Shelton for the use of the SQUID magnetometer. We thank David Webb for useful discussions and John Greedan for his comments on this manuscript. S.B. gratefully acknowledges a U.C. Dissertation Year Fellowship. This research is supported by NSF, Division of Materials Research, DMR-9201041, and the donors of the Petroleum Research Fund administered by the ACS.

#### References

- R.J. Cava, B. Batlogg, J.J. Krajewski, W.F. Peck, Jr. and L.W. Rupp, Jr., J. Less-Common Met., 164-165 (1990) 749.
- [2] A. Adam and H.-U. Schuster, Z. Anorg. Allg. Chem., 584 (1990) 150.
- [3] E. Brechtel, G. Cordier and H. Schäfer, Z. Naturforsch. B, 34 (1979) 777.
- [4] E. Brechtel, G. Cordier and H. Schäfer, Z. Naturforsch. B, 36 (1981) 27.
- [5] S.L. Brock, H. Hope and S.M. Kauzlarich, *Inorg. Chem.*, 33 (1994) 405.
- [6] S.L. Brock and S.M. Kauzlarich, Inorg. Chem., 33 (1994) 2491.
- [7] S.L. Brock and S.M. Kauzlarich, Comm. Inorg. Chem., 4 (1995).
- [8] S.L. Brock and S.M. Kauzlarich, CHEMTECH, 25 (1995) 18.
- [9] N.T. Stetson and S.M. Kauzlarich, Inorg. Chem., 30 (1991) 3969.
- [10] S.L. Brock, N.P. Raju, J.E. Greedan and S.M. Kauzlarich, J. Alloys Comp., 237 (1996) 9.
- [11] C.M. Clark, D.K. Smith and G.A. Johnson, POWDER: A FOR-TRAN IN program for calculating X-ray diffraction patterns, Vers. 5, University Park, PA, 1973.
- [12] E. Parthé and B. Chabot, in K.A. Gschneidner, Jr. and L. Eyring (eds.), Handbook on the Physics and Chemistry of Rare Earths, Vol. 6, Elsevier, New York, 1984, pp. 113-334.
- [13] A. Bondi, J. Phys. Chem., 68 (1964) 441.
- [14] J.A. Kafalas and J.B. Goodenough, Phys. Rev., 157 (1967) 389.
- [15] H. Ido, T. Kaneko and K. Kamigaki, J. Phys. Soc. Jpn., 22 (1967) 1418.
- [16] R. Navarro, J.J. Smit, L.J. de Jongh, W.J. Crama and D.J.W. Ijdo, *Physica B*, 83 (1976) 97.
- [17] M.E. Fisher, Philos. Mag., 17 (1962) 1731.
- [18] R.J. Birgeneau, H.J. Guggenheim and G. Shirane, *Phys. Rev.* B, 1 (1970) 2211.
- [19] B.E. Warren, Phys. Rev., 59 (1941) 693.
- [20] M.E. Lines, J. Phys. Chem. Solids, 31 (1970) 101.
- [21] L.J. de Jongh, in L.J. de Jongh (ed.), Magnetic Properties of Layered Transition Metal Compounds, Kluwer Academic, 1990, p. 19.
- [22] R.J. Carlin and A.J. van Duyneveldt, in *Inorganic Chemistry Concepts*, Vol. 2, Springer, New York, 1977.
- [23] J.A. Mydosh, Spin glasses: an experimental introduction, Taylor & Francis, London, 1993.