

Are optically active three-dimensional oxalate-based ferromagnets good candidates for the observation of x-ray magnetochiral dichroism? A neutron diffraction study

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2008 J. Phys.: Condens. Matter 20 135214

(<http://iopscience.iop.org/0953-8984/20/13/135214>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 11:15

Please note that [terms and conditions apply](#).

Are optically active three-dimensional oxalate-based ferromagnets good candidates for the observation of x-ray magnetochiral dichroism? A neutron diffraction study

Fabrice Pointillart¹, Michel Gruselle¹, Gilles André² and Cyrille Train¹

¹ Laboratoire de Chimie Inorganique et Matériaux Moléculaires, UMR 7071, IFR 2769, UPMC Univ Paris 06, 4 place Jussieu, case 42, F-75252 Paris Cedex 05, France

² Laboratoire Léon Brillouin, CEA-CNRS, CEA/Saclay, F-91191 Gif sur Yvette, France

Received 15 November 2007, in final form 15 February 2008

Published 12 March 2008

Online at stacks.iop.org/JPhysCM/20/135214

Abstract

Neutron diffraction studies have been performed on $[\text{Ru}(\text{bpy})_2(\text{ppy})][\text{MnCr}(\text{ox})]$ (bpy = 2,2'-bipyridine; ppyH = 2-phenylpyridine; ox = oxalate), a 3D oxalate-based compound in one of its optically active forms. The diffraction pattern matches with the $P2_13$ space group found by x-ray diffraction. The magnetic structure has been studied in the magnetically ordered phase of the compound, e.g. below 5.5 K. The compound orders ferromagnetically. Owing to the most probable orientation of the spins, the magnetic space group is $P2_12'_12'_1$. The Shubnikov group is then $22'2'$. Such a magnetic point group is compatible with the observation of x-ray magnetochiral dichroism, the occurrence of a ferromagnetic ordering being an important factor to enhanced the forecast effect.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Multifunctional materials combine several physico-chemical properties. Because these properties may interact, such materials are an ideal source for the observation of new physical properties [1, 2]. Among these, optically active magnets, because they exhibit simultaneous breakings of space-parity and time-reversal symmetries are good candidates to observe an optical effect named magnetochiral dichroism (MChD). This effect has been predicted theoretically and observed on paramagnetic compounds in the visible [1] and on antiferromagnetic compounds in the x-ray region [3]. In both cases, the effect, expected to be small, is very small. A good way to enhance this effect is to use ferro- or ferrimagnetically ordered materials synthesized in their optically active forms. Moreover, the study of new systems will allow a deeper understanding of the effect. But, because the transitions at work in these two spectral regions are different, a given material may not be suitable for observing the phenomenon

both in the visible and x-ray domains. Concerning the x-ray region, using symmetry arguments, Goulon *et al* have precisely found the magnetic point groups (Shubnikov groups) capable of showing this effect [4].

The main interest of the molecular approach to multifunctional materials is in the ability to forecast the final properties of the material by the proper choice of building blocks and its versatility in the choice of constituents with various physico-chemical characteristics. For example, to obtain optically active magnets, it is possible to start from chiral ligands and/or chiral metal complexes used in their resolved forms in order to develop optical activity and bridging ligands able to mediate the exchange interaction in order to favour long range magnetic ordering. We have been studying oxalate-based magnets of general formula $\text{C}[\text{M1M2}(\text{ox})_3]$ (ox = $\text{C}_2\text{O}_4^{2-}$) noted $\text{C}[\text{M1M2}]$. They were described for the first time by Tamaki *et al* [5]. Further reports have shown that these compounds were bi-dimensional (2D) [6, 7] but that they could be obtained as three-dimensional (3D)

compounds as well [8]. Several reviews have shown that the control over dimensionality could generally be achieved through the choice of counteranion C^+ [9–11] while the control over optical activity could be achieved by using either resolved tris(oxalato)metalate building blocks or through enantioselective supramolecular self-assembly, resolved optically active template cations C^{*+} [12–15].

Despite the information it can bring to the comprehension of often complex magnetic structures and/or on the spin density, neutron diffraction has not been extensively used for the study of molecule-based magnets [16–20]. The need for nearly centimetre-scale single crystals and/or fully deuterated samples is undoubtedly a major drawback for coordination chemists. Neutron diffraction of 2D and 3D oxalate-based magnets led to three publications [21–23]. The 2D compounds, one in its ferromagnetic order [22], the other one in an antiferromagnetic (AF) one [23], have been studied in their racemic form. The obtained results have confirmed the magnetometric studies. Special attention has been paid to a 3D compound [21], studied as a racemate, exhibiting an AF exchange coupling between the spin bearers in the hope, not yet achieved, of observing a helical magnetic structure, tentatively chiral [24, 25], associated with the existence of interconnected helices in the crystal structure of the material.

We described hereafter the results obtained by powder neutron diffraction on an optically pure form of a deuterated sample of the ferromagnetic 3D compound [Ru(bpy)₂(ppy)] [MnCr(ox)] (bpy = 2,2'-bipyridine; ppyH = 2-phenylpyridine) first described by Andres *et al* [12]. This study has been performed to determine the magnetic point group of this material in order to figure out whether it is a good candidate to measure enlarged x-ray MChD in a ferromagnetically ordered phase [4] which is the final goal of this project.

2. Experimental section

2.1. General details

All the compounds were prepared according to literature methods [12, 26–30] starting from the corresponding deuterated reagents. Modifications have been brought to the experimental operating mode when needed (see below). Deuterated bromobenzene (d_5 - ϕ Br) and pyridine (C_5D_5N) have been bought from Eurisotop. All the reagents were used as received. The quality of the samples was checked by IR spectroscopy, elemental analysis and powder x-ray diffraction (XRD) by comparison with the published data [12].³

³ The IR spectra were recorded on a Bio-Rad IRFT spectrometer as KBr pellets in the 4000–250 cm^{-1} region. Elemental analyses (C, H, N) were completed at the SIARE-UPMC, Paris. The powder x-ray diffraction patterns were collected at room temperature on a Philips PW-1050 goniometer using the Bragg–Brentano configuration and Mn-filtered Fe $K\alpha$ radiation. The deuteration ratio of bpy was determined by mass spectrometry. Positive chemical ionization mass spectrum, using ammonia as a reagent gas, was recorded with a triple quadrupole instrument (Nermag R 30-10, Quad Service, Poissy, France). 1 μ l of sample solution (1 $g\ l^{-1}$) was left to evaporate on the tungsten filament and was introduced via the direct desorption chemical ionisation probe to the high pressure modified source. After pressure optimization, the source operating conditions were: emission current, 100 mA; repeller voltage, 0 V; electron energy, 70 eV; temperature, $\sim 80^\circ C$. The mass spectrum was an average of 20 scans. Quadrupole scanning was carried out by EZSCAN Data System (Mass Evolution, Houston, TX).

2.2. Synthesis of d_9 -2-phenylpyridine (d_9 -ppy)

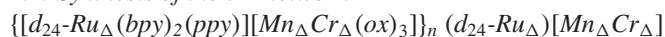
Deuterated d_9 -2-phenylpyridine has been obtained following a modified version of the published synthetic procedure [26, 27].

A solution of 20.9 ml of freshly distilled d_5 -bromobenzene ($M = 161.9\ g\ mol^{-1}$, $d = 1.55$, $n = 0.2\ mol$) in 250 ml of anhydrous ether was added dropwise to 2.931 g of metallic lithium Li^0 ($M = 6.9\ g\ mol^{-1}$, $n = 0.425\ mol$) for 45 min under argon atmosphere. A slight heating of the mixture can be needed to start the reaction (gentle reflux of the ether solution). The appearance of a white cloud within the solution marked the beginning of the reaction. After the end of the addition, 50 ml of anhydrous ether were added. The mixture was stirred until the complete disappearance of the metallic lithium (about 1.5 h). Then a solution of 30 ml of d_5 -pyridine ($M = 84\ g\ mol^{-1}$, $d = 1.05$, $n = 0.375\ mol$) in 80 ml of anhydrous toluene was added under stirring. After the addition, the ether was removed under vacuum and the resulting solution was refluxed for 8 h. After this delay, 30 ml of water were slowly added to the cooled mixture. After filtration, the organic layers were collected and dried by adding 8 g of potassium hydroxide KOH ($M = 56\ g\ mol^{-1}$, $n = 0.14\ mol$). After 1 h of stirring, the mixture was distilled with a short column, first under atmospheric pressure to remove the toluene and then under reduced pressure ($P = 12\ mmHg$). The fractions between 138 and 142 $^\circ C$ were collected to obtain a yellow oil which was purified by chromatography (silica 230–400 mesh, 60 Å ; 1:1 ether/pentane) to afford 12 ml of pure d_9 -2-phenylpyridine as uncoloured oil. Yield: 42%.

2.3. Synthesis of d_8 -2,2'-bipyridine (d_8 -bpy)

The literature method [28] has led to a 90% yield. The deuteration rate has been found to be equal to 91% by mass spectroscopy.

2.4. Synthesis of the 3D network



A slight modification of the literature method [12] of the hydrogenated network $\text{Ru}_\Delta[\text{Mn}_\Delta\text{Cr}_\Delta]$ was used to obtain the deuterated 3D network $(d_{24}\text{-Ru}_\Delta)[\text{Mn}_\Delta\text{Cr}_\Delta]$ in high yield. A solution of 785 mg of $\text{K}_3\text{Cr}_\Delta(\text{ox})_3 \cdot 3\text{H}_2\text{O}$ ($[\alpha_D]^{20} = -1530^\circ$, $C = 0.04\ M$ in H_2O , lit: -1940° , $M = 487\ g\ mol^{-1}$, $n = 1.61\ mmol$) and 392 mg of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ($M = 198\ g\ mol^{-1}$, $n = 1.98\ mmol$, slight excess) in 5 ml of H_2O was added to a solution obtained by dissolving 1.310 g of $d_{24}\text{-[Ru(bpy)}_2(\text{ppy})]\text{PF}_6$ ($M = 712\ g\ mol^{-1}$, $n = 1.84\ mmol$, slight excess) in 5 ml of dimethylsulfoxide. The successive additions of 28 ml of acetone–water–acetone–water–acetone lead to the precipitation of a dark purple solid. After 45 min, the precipitate is filtered off, washed with 20 ml of water and 100 ml of acetone (until an uncoloured filtrate is obtained), and air-dried to yield 1.181 g (76%) of a dark purple solid characterized as $[d_{24}\text{-Ru}_\Delta(\text{bpy})_2(\text{ppy})][\text{Mn}_\Delta\text{Cr}_\Delta(\text{ox})_3]$.

2.5. Neutron diffraction

The neutron diffraction experiments were performed at the Laboratoire Léon Brillouin (CEA Saclay) using the G4.1

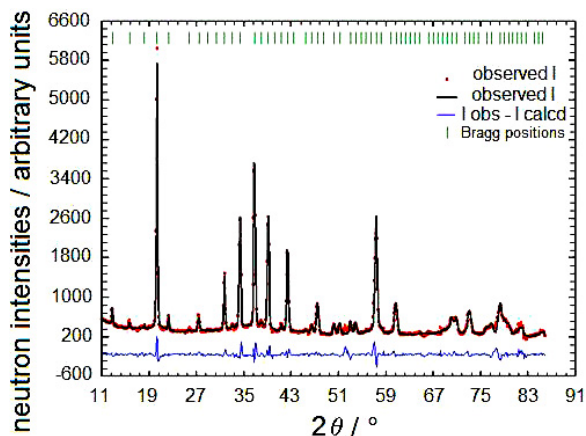


Figure 1. Experimental neutron diffraction pattern (open circles) of a polycrystalline powder of $(d_{24}\text{-Ru}_\Delta)[\text{Mn}_\Delta\text{Cr}_\Delta]$ at $T = 8$ K superimposed with the calculated profile matching plot (continuous line). The difference pattern is shown below.

multi-detector. Data obtained on this powder neutron diffractometer, (800 cells, $\lambda = 2.422$ Å) were used for the refinement of the structural parameters above T_C and the determination of the magnetic structure and its evolution as a function of temperature. Nine diffraction patterns were recorded in the 2θ range 6° – 85.9° , at different temperatures between 1.5 and 15 K. The powder sample was set in a cylindrical vanadium container and held in an orange liquid helium cryostat. Nuclear and magnetic structures were refined using the FULLPROF program [31]. The nuclear scattering lengths and magnetic (Mn^{2+} , Cr^{3+}) form factors were those included in this program.

3. Results and discussions

The powder neutron diffraction (PND) of $(d_{24}\text{-Ru}_\Delta)[\text{Mn}_\Delta\text{Cr}_\Delta]$ whose Curie temperature is 5.8 K [12], has been performed between 1.5 and 15 K. As already stated on an analogous compound [21], no structural phase transition is observed between room temperature and 15 K. The neutron diffraction patterns are composed of thin peaks, indicating a good crystallinity of the deuterated sample. Figure 1 shows the experimental pattern at 8 K together with a profile matching fit performed using the $P2_13$ space group taken from single crystal x-ray diffraction [12]. All the peaks are perfectly indexed and the lattice parameters refined for the cubic unit cell are $a = b = c = 153.535(5)$ Å, $\alpha = \gamma = \beta = 90^\circ$ and $V = 3619.2(2)$ Å³. These structural parameters found by PND are in good agreement with those found by single crystal x-ray diffraction at 300 K for the hydrogenated compound ($a = b = c = 15.368(5)$ Å, $\alpha = \gamma = \beta = 90^\circ$ and $V = 3627(2)$ Å³) [12]. The incomplete deuteration of the template cation together with the indeterminate position of the hydrogen atoms in the compound prevents a complete Rietvelt refinement of the atomic positions in the compound.

When lowering the temperature through the Curie temperature, an increase of the intensities of the peaks is observed but no extra peak appears on the neutron diffraction

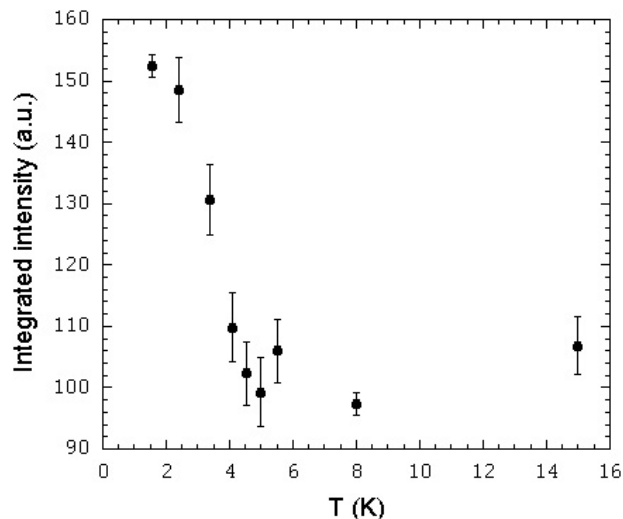


Figure 2. Thermal variation of the integrated intensity of the (110) diffraction peak observed for $2\theta = 12.9^\circ$ for $(d_{24}\text{-Ru}_\Delta)[\text{Mn}_\Delta\text{Cr}_\Delta]$.

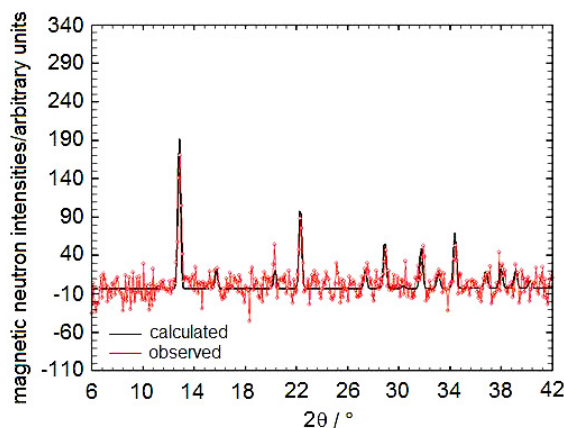


Figure 3. Difference between the diffraction patterns of $(d_{24}\text{-Ru}_\Delta)[\text{Mn}_\Delta\text{Cr}_\Delta]$ measured at 1, 5 and 8 K (open circles) superimposed with the magnetic calculated model (continuous line) obtained with a parallel arrangement of the Mn(II) and Cr(III) magnetic moments.

pattern. The evolution of the intensity is particularly sensitive for the peak observed for $2\theta = 12.9^\circ$ whose Miller indices are (110). The thermal variation of the integrated intensity of the (110) is shown in figure 2 and puts in evidence a magnetic transition at around 5.5 K. This value is in accordance with the 5.8 K Curie temperature found by magnetometry [12].

The increase of the peak intensities is due to a superposition of a magnetic contribution, induced by the long range ordering of the Mn(II) and Cr(III) ions' magnetic moments, to the structural contribution. To isolate the magnetic contribution to the neutron diffraction pattern, we performed the difference between the experimental pattern at 1.5 K, below the Curie temperature and 8 K, above the Curie temperature (figure 3). Because all the magnetic peaks show an origin on structural peaks, the neutron magnetic intensities are calculated in models with a propagation vector $\mathbf{K} = 0$. The difference pattern is then refined letting free the value of

the magnetic moments of all the manganese and chromium atoms of the unit cell (figure 3). This procedure led to a parallel ferromagnetic arrangement of the magnetic moments of all the Mn(II) and Cr(III) ions. The magnetic moment borne by the manganese atoms is $4.6(3) \mu_B$ while it is $2.9(3) \mu_B$ for Cr(III) ions. The calculated pattern is not sensitive to the orientation of the magnetic moments along the C_2 screw axis (x -, y - or z -axis) or along the C_3 -axis of the crystallographic structure, as expected from the cubic symmetry of the studied polycrystalline sample.

It is therefore not possible to determine the magnetic space group unambiguously from neutron diffraction patterns. There must be lowering of the structural symmetry when going in the ferromagnetic phase because the direction taken by the magnetic moments *de facto* defines an axis that breaks the cubic symmetry observed in the paramagnetic phase [32]. Mossbauer studies performed on the iron (III) analogue, $[\text{Ru}(\text{bpy})_2(\text{ppy})][\text{MnFe}(\text{ox})_3]$ showed that the easy axis was along the [100] direction of the cubic structure [33]. The magnetic space group would then be $P2_12'_12'_1$. The compound $(d_{24}\text{-Ru}_\Delta)[\text{Mn}_\Delta\text{Cr}_\Delta]$ can then be described in the $22'2'$ Shubnikov group⁴.

The magnetic moment values carried by the metal ions are, within the precision of the presented experiment, compatible with the spin-only values expected, taking into account the isotropic character of the Mn(II) and Cr(III) ions in an octahedral environment. Finally, following the symmetry analysis of Goulon *et al* [4], the $22'2'$ Shubnikov group observed for $(d_{24}\text{-Ru}_\Delta)[\text{Mn}_\Delta\text{Cr}_\Delta]$ in its ferromagnetic phase is compatible with the observation of XMChD due to the existence of three non-vanishing contributions to the XMChD.

4. Concluding remarks

Neutron diffraction studies have been performed on a 3D oxalate-based magnet in one of its optically active forms. In its magnetically ordered phase, it can tentatively be described in the $22'2'$ Shubnikov group. Such a group is compatible with the observation of XMChD [4]. Another candidate to observe this effect would be the 2D oxalate-bridged analogues. When they are synthesized in their optically active forms, they crystallize in the $P6_3$ space group. Upon ferromagnetic ordering with easy-magnetization axis parallel to the hexagonal axis, they are expected to belong to the 6 Shubnikov group. Such a group is compatible with a non-vanishing $\Omega^{(1)}$ anapole, which is the main contribution to the XMChD [4]. A neutron diffraction study will be needed to confirm the Shubnikov group of these parent compounds in their magnetically ordered phase.

As known for more than a century, the optical activity of chiral compounds can be observed only if the sample is enantiomerically pure or, at least, enriched. For the same reason, observing the effects derived from simultaneous

breakings of space-parity and time-reversal symmetries requires enantiomerically pure (or enriched) materials. In the visible region, such effects can be seen even on powders or solutions [1]. In the x-ray region, the electric dipole–electric quadrupole phenomenon dominates the effect. It imposes severe symmetry restrictions at the crystal level [4]. XMChD has been observed in an antiferromagnetic compound [1, 3]. The effect is then very small. The present work opens the perspective to observe a much larger XMChD because: (i) the overall symmetry prevents the cancellation of the effect (ii) the optical activity is well controlled and (iii) the ferromagnetic order ensures that the local magnetic moments carried by the two metal ions are all aligned in the same direction. Moreover, the versatility of the molecular approach of multifunctional materials towards metal ion substitution in the oxalate-based network can allow us to tune both the nature of the exchange interaction and the orbital contribution of the constituents. The influence of these determining factors on the XMChD can thus be studied to ensure a deeper understanding of this effect.

Acknowledgments

The authors are grateful to Dr P Gredin for powder XRD experiments, Dr D Lesage for mass spectrometry measurements and Dr Ch Cartier dit Moulin for fruitful scientific discussions. The authors thank CNRS (France), UPMC Univ Paris 06 (France) and DFG (SPP 1137) for financial support.

References

- [1] Rikken G L J A and Raupach E 1997 *Nature* **390** 493
- [2] Spaldin N A and Fiebig M 2005 *Science* **309** 391
- [3] Goulon J, Rogalev A, Wilhem F, Goulon-Gibet C, Carra P, Cabaret D and Brouder C 2002 *Phys. Rev. Lett.* **88** 237401
- [4] Goulon J, Rogalev A, Wilhem F, Goulon-Gibet C, Carra P, Marri I and Brouder C 2003 *JETP* **97** 402
- [5] Tamaki H, Zhong Z J, Matsumoto N, Kida S, Koikawa M, Achiwa N, Hashimoto Y and Okawa H 1992 *J. Am. Chem. Soc.* **114** 6974
- [6] Atovmyan L O, Shilov G V, Lubovskaya R N, Zhilyaeva E I, Ovanesyan N S, Pirumova S I, Gusakovskaya I G and Morozov Y G 1993 *J. Exp. Theor. Phys. Lett.* **58** 766
- [7] Decurtins S, Schmalle H W, Oswald H R, Linden A, Ensling J, Guetlich P and Hauser A 1994 *Inorg. Chim. Acta* **216** 65
- [8] Decurtins S, Schmalle H W, Schneuwly P, Ensling J and Guetlich P 1994 *J. Am. Chem. Soc.* **116** 9521
- [9] Decurtins S, Pellaux R, Antorrena G and Palacio F 1999 *Coord. Chem. Rev.* **190–192** 841
- [10] Pilkington M and Decurtins S 2001 *Magnetism: Molecules to Materials* vol II, ed J S Miller and M Drillon (Weinheim: Wiley–VCH) p 339
- [11] Clement R, Decurtins S, Gruselle M and Train C 2003 *Monatsh. Chem.* **134** 117
- [12] Andres R, Brissard M, Gruselle M, Train C, Vaissermann J, Malezieux B, Jamet J-P and Verdaguer M 2001 *Inorg. Chem.* **40** 4633
- [13] Gruselle M, Thouvenot R, Malezieux B, Train C, Gredin P, Demeschik T V, Troitskaya L L and Sokolov V I 2004 *Chem. Eur. J.* **10** 4763
- [14] Gruselle M, Train C, Boubekeur K, Gredin P and Ovanesyan N S 2006 *Coord. Chem. Rev.* **250** 2491

⁴ Another possibility, not yet experimentally demonstrated on such compounds, would be an orientation of the easy axis along one of the four three-fold axes of the cubic structure. The symmetry is then lowered to $R3$ and the corresponding magnetic point group is 3. This Shubnikov group is compatible with the observation of XMChD as well as $22'2'$ [4].

- [15] Pointillart F, Train C, Boubekour K, Gruselle M and Verdaguier M 2006 *Tetrahedron Asymmetry* **17** 1937
- [16] Ressouche E 1999 *Physica B* **268** 27
- [17] Schweizer J 1997 *Physica B* **234** 772
- [18] Baron V, Gillon B, Cousson A, Mathonière C, Kahn O, Grand A, Öhrström L, Delley B, Bonnet M and Boucherle J X 1997 *J. Am. Chem. Soc.* **119** 3500
- [19] Gillon B 2001 *Magnetism: Molecules to Materials* vol 1, ed J S Miller and M Drillon (Weinheim: Wiley-VCH) p 357
- [20] Gillon B, Goujon A, Willemin S, Larionova J, Desplanches C, Ruiz E, André G, Stride J A and Guérin C 2007 *Inorg. Chem.* **46** 1090
- [21] Decurtins S, Schmalle H W, Pellaux R, Huber R, Fischer P and Ouladdiaf B 1996 *Adv. Mater.* **8** 647
- [22] Pellaux R, Schmalle H W, Huber R, Fischer P, Hauss T, Ouladdiaf B and Decurtins S 1997 *Inorg. Chem.* **36** 2301
- [23] Visser D, Carling S G, Watts I D, Day P and Andersen K H 1999 *J. Appl. Phys.* **85** 5378
- [24] Herpin A 1968 *Théorie du Magnétisme* Presses Universitaires de France, Paris
- [25] Adachi K, Achiwa N and Mekata M 1980 *J. Phys. Soc. Japan* **49** 545
- [26] Dupiest M T, Schmidt C L, Kuzmich D and Williams S B 1986 *J. Org. Chem.* **51** 2021
- [27] Gilman H and Edward J T 1953 *Rev. Can. Chim.* **31** 457
- [28] Browne W R, O'Connor C M, Killeen J S, Guckian A L, Burke M, James P, Burke M and Vos J G 2002 *Inorg. Chem.* **41** 4245
- [29] Sullivan B P, Salmon D J and Mayer T J 1978 *Inorg. Chem.* **17** 3334
- [30] Constable E C and Holmes J M 1986 *J. Organomet. Chem.* **301** 203
- [31] Rodriguez-Carvajal J and Roisnel T 1991 *The IUCr Commission on Powder Diffraction of the XV Congr. of the IUCr (Toulouse)* unpublished
- [32] Laughlin D E, Willard M A and Mac Henry M E 2000 *Phase Transformations and Evolution in Materials* ed P Turchi and A Gonis (Warrendale, PA: Minerals, Metals and Materials Society) p 121
- [33] Ovanesyanyan N S, Gruselle M and Train C 2007 unpublished