Spin gap formation in the quantum spin systems TiOX, X = Cl and Br

P Lemmens\textsuperscript{1,2}, K Y Choi\textsuperscript{3}, R Valentí\textsuperscript{4}, T Saha-Dasgupta\textsuperscript{5}, E Abel\textsuperscript{6}, Y S Lee\textsuperscript{6} and F C Chou\textsuperscript{7}

1 Max Planck Institute for Solid State Research, D-70569 Stuttgart, Germany
2 Institute for Physics of Condensed Matter, Technical University of Braunschweig, D-38106 Braunschweig, Germany
3 Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
4 Institute für Theoretische Physik, Universität Frankfurt, D-60054 Frankfurt, Germany
5 S.N. Bose National Centre for Basic Sciences, Salt Lake City, Kolkata 700098, India
6 Department of Physics, MIT, Cambridge MA 02139, USA
7 Center for Materials Science and Engineering, MIT, Cambridge MA 02139, USA

E-mail: p.lemmens@tu-bs.de

New Journal of Physics 7 (2005) 74
Received 4 January 2005
Published 2 March 2005
Online at http://www.njp.org/
doi:10.1088/1367-2630/7/1/074

Abstract. In the layered quantum spin systems TiOCl and TiOBr, the magnetic susceptibility shows a very weak temperature-dependence at high temperatures and transition-induced phenomena at low temperatures. There is a clear connection between the observed transition temperatures and the distortion of the octahedra and the layer separation. Band structure calculations point to a relation between the local coordinations and the dimensionality of the magnetic properties. While from magnetic Raman scattering only a small decrease of the magnetic exchange by \(-5\) to \(10\%\) is derived comparing TiOCl with TiOBr, the temperature dependence of the magnetic susceptibility favours a much bigger change.
1. Introduction

The compounds TiOX, with X = Cl and Br are formed by layers of distorted TiO$_4$X$_2$ octahedra. Quantum magnetism in these systems is based on the Ti$^{3+}$ ions with one electron (3d$^1$, s = 1/2) in a t$_{2g}$ state. The distortion of the octahedra leads to the predominant occupation of d$_{xy}$ orbitals that form chain-like direct exchange paths of orbitals along the crystallographic b-axis of the compound. These systems belong to a new class of spin-1/2 transition metal oxides based on Ti$^{3+}$ ions in weakly interconnected, distorted octahedral coordinations [1]–[4]. Very often these titanates show phase transitions into singlet ground states that resemble the spin-Peierls instability. In contrast to, e.g. CuGeO$_3$ [5] where the spin-Peierls transition leads to a mean-field size of the reduced gap ratio, very large spin gaps exist in some titanates [2, 6]. For TiOCl, even a pseudo gap for $T > T_c$ has been reported based on NMR and Raman scattering experiments [7, 8]. Since the t$_{2g}$ states of the Ti$^{3+}$ ions show orbital degeneracy in a perfect octahedral surrounding, it is tempting to assign part of these phenomena to orbital degrees of freedom.

In several experiments like magnetic susceptibility [3, 9], NMR [7], ESR [10], x-ray scattering [11, 12], Raman scattering and optical spectroscopy [8, 13], strong fluctuations and multiple transitions are observed that are attributed to this spin–orbital system with low dimensionality. Instabilities in spin–orbital coupled systems have been investigated theoretically [14]–[17] since they are candidates for exotic electronic configurations [3, 9, 17]. However, these theoretical scenarios did not explicitly consider static or dynamic phonon degrees of freedom. For two-dimensional (2D) systems with low symmetry exchange paths, it is known that phonons stabilize spin liquids and shift phase lines [18]. Furthermore, orbital configurations strongly couple to the lattice. Therefore, changes of lattice parameters are expected to affect the magnetic properties and related instabilities of such systems considerably.

So far, with the exception of one IR investigation [19], only the system TiOCl has been investigated thoroughly. The isostructural TiOBr has not been at the centre of interest due to more severe problems in growing single crystalline samples of sufficient quality. The scaling of IR active phonon frequencies with the involved ionic masses, however, proposes TiOBr as a perfect reference system.

In this paper, we present a comparative study of TiOCl and TiOBr using magnetic susceptibility, Raman scattering and band structure calculations to relate structural and electronic properties of these systems and to achieve a better understanding of the observed instabilities. It is shown that the fluctuation regime in TiOBr is even more extended compared to TiOCl.
2. Crystal structure and sample preparation

The layered crystal structure of TiOX is shown in figure 1. The TiX$_2$O$_4$ octahedra share edges and form double layers in the $ab$ plane of an orthorhombic unit cell with FeOCl-type structure [20, 21]. Figure 1(a) shows a sketch of the octahedra within two rows of the double layer. In figures 1(b) and (c) local Ti-O-X coordinations are given in the $bc$ and the $ab$ plane, respectively. Important structural parameters and atomic distances are given in Table 1. It is evident that the substitution of Cl by Br leads to a considerable increase in the volume of the unit cell. The $c$-axis lattice parameter changes from 8.03 to 8.53 Å, going from X = Cl to Br what implies that in TiOBr the coupling between the planes of octahedra is even less important compared to TiOCl. The $b$ parameter also shows a small increase from 3.38 to 3.49 Å. Furthermore, the distortion of octahedra is larger in TiOBr. This is demonstrated in Table 1 by comparing the shift of the Ti ion out of the basal plane of the octahedra along the $c$-axis.

Single crystals of TiOCl and TiOBr have been grown using a chemical vapour transport method [3]. In the following, we will describe the preparation of TiOBr as it is less well established. An initial mixture of TiO$_2$, Ti and TiBr$_4$ with a molar ratio of 4 : 3 : 9 was sealed in an evacuated quartz tube. The tube was then placed within a two-zone furnace, and a constant thermal gradient was maintained (650 to 550 °C over a 25 cm distance). After approximately 5–8 days, single crystals of TiOBr with sizes up to 5 mm$^2$ can be extracted. The quality of the TiOBr crystals is similar to the TiOCl crystals investigated in [3]. However, TiOBr is less stable under ambient conditions, as it readily reacts with water in the air.

The magnetic susceptibility has been measured on a single crystal sample of TiOBr using a SQUID magnetometer. Raman scattering investigations have been performed using the 514.5 nm excitation wavelength with light polarization parallel to the crystallographic $b$-axis of the platelet-like ($ab$ surface) single crystals of TiOCl [3]. No strong resonance effects have been detected comparing 514.5 and 488 nm excitation wavelengths. A comparison of the phonon spectrum of TiOBr with TiOCl using optical reflectivity $R(\omega)$ experiments can be found in [19].
Table 1. Structural parameters and atomic separations for TiOCl and TiOBr with Pmmn (no 59). Units are Å or Å³. Parameters are rounded for clarity and derived using [20, 21]. Intra-layer Ti–Ti separations are given along the direct exchange path parallel to the b-axis and from the upper to the lower Ti site of one double layer. For the inter-layer Ti–Ti separations also two values exist due to the double layers. The distortions of the octahedra are characterized by $\Delta c_{Ti}$, corresponding to the c-axis shift of the Ti ion out of its basal plane.

| Lattice parameters | TiOCl | TiOBr | $10^2 \times \Delta x/x$ |
|--------------------|-------|-------|------------------------|
| Unit cell          |       |       |                        |
| a                  | 3.79  | 3.79  | ±0.0                   |
| b                  | 3.38  | 3.49  | ±3.3                   |
| c                  | 8.03  | 8.53  | ±6.2                   |
| Volume             | 102.9 | 112.6 | ±9.4                   |
| Intra-double layer |       |       |                        |
| Ti–Ti              | 3.38  | 3.49  | ±3.2                   |
| Ti–Ti_{bc}         | 3.2   | 3.19  | ±0.3                   |
| Inter-double layer |       |       |                        |
| Ti–Ti              | 6.58  | 7.12  | ±8.2                   |
| Ti–Ti_{bc}         | 8.13  | 8.91  | ±9.6                   |
| Distortion $\Delta c_{Ti}$ | $5.5 \times 10^{-2}$ | $6.1 \times 10^{-2}$ | ±10.9 |

related to optical experiments can be found in [22]. A review of the implications of magnetic Raman scattering in low-dimensional spin systems is given in [5].

3. Magnetic susceptibility and phase transitions

In figure 2, the magnetic susceptibility $\chi(T)$ of TiOBr is given. The open circles are the raw data, and the filled squares are the data after subtraction of a small Curie tail. The general behaviour is reminiscent of the susceptibility of TiOCl [3, 7] in the sense that above 100 K the magnetic susceptibility $\chi(T)$ of TiOBr is only weakly temperature dependent [9] and forms a broad maximum at $T_{\text{max}} \sim 210$ K. In contrast to TiOCl, the Bonner–Fisher curve does not provide a good fit to the higher temperature behaviour of TiOBr (not shown here).

At low temperatures, there is a dramatic drop in the susceptibility at $T_{c1}^{Br} = 28$ K. X-ray scattering in TiOCl has revealed a commensurate dimerization for $T < T_{c1}^{Cl} = 67$ K along the b-axis [11, 12]. Thereby, the crystal structure changes from Pmmn to P2\textsubscript{1}/m with atomic displacements restricted to the bc plane. The flat susceptibility for $T < T_{c1}$ is therefore taken as an indication for a similar structural distortion in TiOBr that accompanies the spin gap formation. It has been highlighted that, with the exception of the relatively large spin gap, the resulting low temperature state of the two systems is very well comparable to other spin-Peierls systems [8, 13].

The inset in figure 2 shows the normalized susceptibility $(\chi - \chi_0)/\chi_{\text{max}}$ of both systems versus $T_{c1}$ and versus $T_{c2}$ of the respective compound. $\chi_0$ has been extrapolated in the limit $T \to 0$. From these data, it is evident that the overall susceptibilities scale very well with respect to $T_{c1}$. This refers mainly to the decrease that is observed towards lower temperatures. Smaller deviations exist in the temperature regime $T_{c1} < T < 2T_{c1}$ and a close inspection of
the susceptibility data reveals a second critical temperature $T_{c_2}^{Br} = 47$ K at which the change of susceptibility is most pronounced. At the corresponding temperature $T_{c_2}^{Cl} = 92$ K of TiOCl, evidence for incommensurate distortions has been found together with anomalies in the specific heat [11]. Some results of the magnetic characterization are summarized in table 2.

In the lower inset of figure 2, the magnetic susceptibility is plotted with respect to the higher characteristic temperature. The decrease in the magnetic susceptibility does not scale well with $T_{c_2}$. As this decrease is related to the opening and magnitude of the spin gap $\Delta (T)$ at the respective temperature, $T_{c_2}$ cannot be directly related to the spin gap formation.

**Figure 2.** Magnetic susceptibility $(M/H)$ of TiOBr with a magnetic field of 1 tesla parallel to the $ab$ plane. Open (full) symbols correspond to the measured data (data after subtracting a defect contribution). The upper and lower insets show the scaled susceptibility $(\chi - \chi_0)/\chi_{\text{max}}$ versus $T/T_{c_1}$ or versus $T/T_{c_2}$ for TiOX, $X = \text{Cl}$ and $\text{Br}$. The transition temperatures are given in table 2.

**Table 2.** Magnetic parameters from TiOCl and TiOBr determined from susceptibility, the maxima positions in Raman scattering data, the exchange coupling parameters from downfolding the bandstructure and their change in % with respect to TiOCl.

|           | TiOCl | TiOBr | $10^2 \times \Delta \chi/\chi$ |
|-----------|-------|-------|---------------------------------|
| $T_{c_1}$ | 67 K  | 28 K  | $-58.2$                         |
| $T_{c_2}$ | 92 K  | 47 K  | $-48.9$                         |
| $T_{\text{max}}$ in $\chi (T)$ | 400 K | 210 K | $-47.5$                         |
| $T_{c_1}/T_{\text{max}}$ | 0.16 | 0.13 | $-$                              |
| $T_{c_2}/T_{\text{max}}$ | 0.23 | 0.22 | $-$                              |
| $\Delta \omega_{\text{max}}^1$ | 928 cm$^{-1}$ | 875 cm$^{-1}$ | $-5.7$                         |
| $\Delta \omega_{\text{max}}^2$ | 1404 cm$^{-1}$ | 1390 cm$^{-1}$ | $-1.0$                         |
| $J_d^{\text{downfolding}}$ | 621 K | 406 K | $-35$                              |
Table 3. Predominant hopping integrals (in eV) $t_{i,j}$ for TiOCl and TiOBr obtained from downfolding the bandstructure results (see text). In the table, only the significant digits have been given.

| Ti–Ti hopping integrals | TiOCl | TiOBr | $10^2 \times \Delta x/x$ |
|-------------------------|-------|-------|--------------------------|
| t n.n. hopping along $b$| -0.21 | -0.17 | -19                      |
| $t'$ n.n. hopping along $a$, same layer | 0.04  | 0.06  | +50                      |
| $t''$ n.n. hopping along $a$, different layers | 0.03  | 0.04  | +33                      |

The scaling behaviour may be further investigated by comparing ratios of the critical temperatures and the maxima of the susceptibility $\chi(T)$. The maximum in $\chi(T)$ gives some information about an averaged magnetic coupling strength. According to Cross and Fisher [23], a linear relation between $T_c$ and the exchange coupling $J$ is expected for spin-Peierls systems with $T_c/J = 0.8\lambda$ and a spin phonon coupling $\lambda$. In table 2, the corresponding ratios are given. It is noteworthy that in contrast to the decrease of the susceptibility its maximum position scales with the higher transition temperature. Comparing these characteristic temperatures the following ratios are determined: $T_{c1}^{Cl}/T_{c1}^{Br} = 2.4$, $T_{c2}^{Cl}/T_{c2}^{Br} = 1.96$, while the maximum temperatures give $T_{\text{max}}^{Cl}/T_{\text{max}}^{Br} = 1.91$. Especially, the latter two ratios show a good matching and lead to the conclusion that the characteristic energy scales of the thermodynamic quantities differ roughly by a factor of two between the two systems. This conclusion does not perfectly match with the calculated hopping integral $t$ given in table 3 and with the results from high-energy Raman scattering discussed below.

For TiOCl, large fluctuations have been reported at high temperatures ($T > T_{c1}$) based on anomalies in the $^{47,49}$Ti spin relaxation rate and a strong temperature dependence of the ESR-derived $g$-factor [7, 10]. These observations lead to the assignment of a fluctuation or pseudo gap temperature at $T^* = 135$ K. For the temperature regime $T_{c1} < T \leq T^* = 135$ K also, pronounced anomalies and softenings of the Raman-active optical phonon modes exist [8]. Furthermore, the spin gap $E_g = 430$ K determined from NMR [7] is very large. The reduced gap ratios are $2E_g/k_B T_{c1,c2} = 10–15$.

4. High-energy Raman scattering

In figure 3, the Raman scattering intensity of TiOCl ($T = 5$ K) and TiOBr ($5$ K $< T < 200$ K) is given in the frequency regime that is characteristic of magnetic scattering. Typical energies of two-magnetic exchange scattering are estimated within an Ising-like picture counting the number of broken bonds that an exchange process leaves behind. Using the coupling constant $J = 660$ K for TiOCl from magnetic susceptibility [3], magnetic light scattering should have typical energies between $2J = 920$ cm$^{-1}$ and $4J = 1800$ cm$^{-1}$. The exchange paths considered theoretically have both 1D and 2D aspects [24]. For TiOCl two broad maxima are observed, a symmetric one at $928$ cm$^{-1}$ ($2J = 917$ cm$^{-1}$) and an asymmetric one at $1404$ cm$^{-1}$ ($3J = 1375$ cm$^{-1}$). For TiOBr, the overall spectral distribution of scattering intensity has a similar shape. The maxima are at $\Delta \omega_{\text{max}}^{Br^{-1}} = 875$ cm$^{-1}$ and $\Delta \omega_{\text{max}}^{Br^{-2}} = 1390$ cm$^{-1}$, i.e. they are shifted by 5 and 1%, respectively, to lower frequencies. At low and intermediate energies, pronounced oscillations or superstructures
are observed with peak frequencies $\Delta \omega_{\text{Br}}^{\text{max}} = 695, 763, 825$ and 883 cm$^{-1}$. These structures have a mean separation of 63 cm$^{-1}$ and are even more pronounced compared to TiOCl.

The double peak structure with additional modulations at low and intermediate energies is a complex structure compared to the observations in other 1D or 2D quantum spin systems. The line shape of such scattering intensity is usually a result of strong magnon–magnon interactions and the local exchange topology. Magnon–magnon interaction leads to a characteristic renormalization and broadening of the spectral weight to lower energy [25].

In undoped high-temperature superconductors with CuO$_2$ planes that represent a 2D $s = 1/2$ Heisenberg magnet, a single, broadened peak with a maximum at $\Delta \omega_{\text{HTSC}}^{\text{max}} \approx 2.8J$ is observed [26]. Also in Cu$_2$Te$_2$O$_5$Br$_2$, a system based on weakly coupled spin tetrahedra, a single symmetric maximum has been observed at $\Delta \omega_{\text{max}} \approx 2J$ [27, 28]. Well-defined double-peak structures have, however, been observed in the 2D nickelates La$_{2-x}$Sr$_x$NiO$_{4+d}$ if stripe domains with a modulation of spin/charge exist. The two maxima in this system are then attributed to exchange processes across and within the antiferromagnetic domain walls and they are related to the exchange coupling as multiples $3J$ and $4J$ for a Sr doping of $x = 1/3$ [29]–[31]. For TiOCl, recent structural investigations also give evidence for a more complex structure of dimerized Ti sites [11]. It is proposed that antiphase domain walls exist within the $ab$ planes that separate nanodomains of different dimer orientations. These situations resemble to some extent, the situation in the 2D nickelates and is proposed to be the reason for the two maxima.

In the respective frequency range, excitations of other origin may also contribute. Here, multi-phonon scattering or magnon–phonon coupled modes [32] should be discussed. Multi-phonon scattering is frequently observed in isolating transition metal oxides and leads to peak structures with frequencies very close to multiples of the optical phonon frequencies. For TiOCl, the Raman allowed phonon modes of the high-temperature phase consist of in-phase Cl–Ti (203 cm$^{-1}$), O–Ti (365 cm$^{-1}$) and O–Cl (430 cm$^{-1}$) modes. The latter mode has an out-of-phase Ti contribution [33]. The numbers in brackets give the respective frequencies for TiOCl.
Raman-active modes and also the IR-active phonon modes soften considerably with the exchange of Cl by Br following simple scaling relationships [19]. For TiOBr the respective Raman modes are observed at 144, 323 and 413 cm\(^{-1}\),\(^8\) which correspond to decrease in the phonon frequencies 4–29%. It is also expected that the phonon dispersion is less pronounced in TiOBr due to the weaker interplane coupling.

In the high-energy regime, on comparing TiOCl with TiOBr no considerable shift is observed, therefore a dominant contribution of multiphonon scattering to the two maxima is not suggested. Furthermore, the corresponding multiples of the phonon frequencies do not exist in the high-energy Raman spectral range. This statement should be softened with respect to the modulations seen on the left shoulder of the first more symmetric maximum. It has been shown for TiOCl that this modulation has the same frequency as the difference between two optical phonon frequencies [8]. Finally, the large energy of orbital excitations (0.3–0.7 eV) should also rule out a direct contribution of this degree of freedom to the observed double peak structure.

5. Ab initio calculations

To investigate the electronic properties of TiOX, we carried out density functional calculations for TiOBr and compared with the results obtained for TiOCl [3, 24]. We performed our ab initio study in the local density approximation (LDA), the generalized gradient approximation (GGA) [34] and in the so-called LDA + U [35] by using the linearized muffin tin orbital (LMTO) method based on the Stuttgart TBLMTO-47 code [36]. The results within LDA and GGA did not lead to significant differences. An analysis of the TiOBr bandstructure (see figure 4) shows that the shape

\(^{8}\) A complete discussion of the phonon spectrum of TiOBr will be published elsewhere.
Figure 5. LDA + U bandstructure of TiOCl (solid red line) and TiOBr (dashed blue line) along the path $\Gamma - X - S - Y - \Gamma - Z$. Note the opening of the gap at the Fermi level with respect to the LDA results. The two bands right below $E_F$ are of Ti-$d_{xy}$ nature.

of the LDA-$t_{2g}$ bands crossing the Fermi level have almost identical dispersions to TiOCl [3, 24], which indicates that the exchange paths are similar between these two compounds. Nevertheless, in TiOBr there is a narrowing of the bandwidth along the $Y - \Gamma - Z$ path, which is a consequence of the enlargement of the cell in $b$ and $c$ directions.

The calculation within the LDA + U approach shows for TiOBr Ti-$d_{xy}$ to be the groundstate as in TiOCl (see figure 5). In order to get a reliable estimate of the interaction paths in TiOBr, we applied the tight-binding-downfolding procedure [24, 37] which obtains the effective Ti-$d_{xy}$ hopping parameters by downfolding all the degrees of freedom in the bandstructure calculation other than Ti-$d_{xy}$. The predominant hopping path in TiOX, $t$, is along the nearest neighbour (n.n.) Ti-$d_{xy}$ in the $b$ direction. $t = -0.21$ eV for TiOCl while $t = -0.17$ eV for the Br system. This reduction reflects the narrowing of the bands in TiOBr.

A rough estimate of the antiferromagnetic superexchange along $b$ can be obtained by using the expression $J = 4t^2/U$ which for $U = 3.3$ eV is $J \approx 621$ K for TiOCl and $J \approx 406$ K for TiOBr. This change is larger than the shift seen in high-energy Raman spectra and in qualitative agreement with the susceptibility measurements. Since we are here interested in estimating the differences between TiOCl and TiOBr, we present in table 3 a detailed account of all relevant effective hopping parameters between Ti-$d_{xy}$–Ti-$d_{xy}$. We observed that the hopping integrals along paths other than $t$ are almost an order of magnitude smaller than the main hopping along $b$; nevertheless, the TiOBr compound has slightly larger effective hoppings along the $ab$ plane than TiOCl, which indicates that, in that system, the interactions within the $ab$ plane may be more significant than in TiOCl. Comparison with table 2 shows that this result is in qualitative agreement with the trend seen in the maximum of the magnetic susceptibility.
6. Summary and conclusions

The system TiOX, with X = Cl and Br, shows a rich spectrum of anomalies related to electronic, spin and structural degrees of freedom that goes far beyond the scenario of usual spin-Peierls materials [23]. Analysis of the magnetic susceptibility and phase diagram demonstrates that the low-temperature transition, $T_{c1}$, connected with a commensurate structural distortion, scales with the decrease of the susceptibility and the evolution of the spin gap. The high-temperature transition, $T_{c2}$, scales with the maximum in the susceptibility that is itself related to the characteristic energy scale of the magnetic system.

The deviations between the latter energy scale and the high-energy Raman scattering are either due to a complex structure of the dimer formation, in analogy with the microscopic stripe formation in $(La, Sr)_{2}NiO_{4+d}$, or due to an interplay with the phonon sector. Due to the strong distortion and the already weak interlayer coupling in TiOCl we do not expect that changes in the dimensionality play an essential role.

Finally, our band structure calculations have shown that, although the effective Ti-d$_{xy}$–Ti-d$_{xy}$ hopping parameters are renormalized with the substitution of Cl by Br, the electronic spectrum does not change drastically. This is in accordance with the high-energy Raman scattering. Following the Cross–Fisher scaling, the difference in the transition temperatures of the two compounds should then be attributed both to the smaller electronic bandwidth and a modified spin–phonon coupling. This scenario, however, is not complete since it neither explains the strong fluctuations nor the large spin gap observed even above the transition temperatures. Further studies on both systems are needed to elucidate these points.

Acknowledgments

The authors acknowledge fruitful discussions with C Gros, H Rosner, L Degiorgi, G Caimi, E Ya Sherman, R Kremer and B Keimer. One of us (TSD) would like to thank the Max Planck Institute–India partner group program for the collaborative support. This work was supported by the MRSEC Program of the National Science Foundation under the award number DMR 02-13282 and DFG SPP1073.

References

[1] Axtell E A, Ozawa T, Kauzlarich S M and Singh RR P 1997 *J. Solid State Chem.* 134 423
[2] Isobe M, Ninomiya E, Vasil’ev A V and Ueda Y 2002 *J. Phys. Soc. Japan* 71 1423
[3] Seidel A, Marianetti C A, Chou F C, Ceder G and Lee P A 2003 *Phys. Rev.* B 67 020405
[4] Isobe M and Ueda Y 2002 *J. Phys. Soc. Japan* 71 1848
[5] Lemmens P, Güntherodt G and Gros C 2003 *Phys. Rep.* 375 1 and references therein
[6] Lemmens P and Millet P 2004 Spin–orbit–topology, a triptych *Quantum Magnetism (Lecture Notes in Physics vol 645)* (Heidelberg: Springer) pp 433–77
[7] Imai T and Chou F C 2003 *Preprint* cond-mat/0301425
[8] Lemmens P, Choi K-Y, Caimi G, Degiorgi L, Kovaleva N N, Seidel A and Chou F C 2004 *Phys. Rev.* B 70 134429
[9] Beynon R J and Wilson J A 1993 *J. Phys.: Condens. Matter* 5 1983
[10] Kataev V, Baier J, Möller A, Jongen L, Meyer G and Freimuth A 2003 *Phys. Rev.* B 68 140405
[11] Abel E, Lee Y S and Chou F C 2004 Personal communication
[12] Shaz M, Smaal S, Palatinus L, Hoinkis M, Klemm M, Horn S and Claessen R 2004 *Preprint* cond-mat/040702
[13] Caimi G, Degiorgi L, Kovaleva N N, Lemmens P and Chou F 2004 Phys. Rev. B 69 125108
[14] Pati S K, Singh R R P and Khomskii D I 1998 Phys. Rev. Lett. 81 5406
[15] Yamashita Y, Shibata N and Ueda K 2000 J. Phys. Soc. Japan 69 242
[16] Koleshuk A K, Mikeska H-J and Schollwöck U 2001 Phys. Rev. B 63 064418
[17] Hikihara T and Motome Y 2004 Preprint cond-mat/0404730
[18] Starykh O A, Zhitomirsky M E, Khomskii D I, Singh R R P and Ueda K 1996 Phys. Rev. Lett. 77 2558
[19] Caimi G, Degiorgi L, Lemmens P and Chou F 2004 J. Phys.: Condens. Matter 16 5583
[20] Schaefer H, Wartenpufhl F and Weise E 1958 Zeit. Allg. Anorg. Chem. 295 268
[21] Schaefer H, von Schnieering H G, Tillock J, Kuhnen F, Wohrle H and Baumann H 1967 Z. Anorg. Chem. 353 281
[22] Caimi G, Degiorgi L, Kovaleva N N, Lemmens P and Chou F C 2004 Phys. Rev. 69 125108
[23] Cross M C and Fisher D S 1979 Phys. Rev. B 19 402
[24] Saha-Dasgupta T, Valentí R, Rosner H and Gros C 2004 Europhys. Lett. 67 63
[25] Brenig W and Becker K W 2001 Phys. Rev. B 64 214413
[26] Sugai S 2000 Magneto-Optics vol 128, ed S Sugano and N Kojima (New York: Springer) pp 75–106, ch 3 (Raman spectroscopy of Magnetic Compounds with Strong Electron-Correlation) and references therein
[27] Lemmens P et al 2001 Phys. Rev. Lett. 87 227201
[28] Gros C et al 2003 Phys. Rev. B 67 174405
[29] Yamamoto K, Katsufuji T, Tanaba T and Tokura Y 1998 Phys. Rev. Lett. 80 1493
[30] Blumberg G, Klein M V and Cheong S-W 1998 Phys. Rev. Lett. 80 564
[31] Gnezdilov V P, Yeremenko A V, Pashkevich Y G, Lemmens G G P, Tranquada J M, Buttrey D J and Nakajima K 2002 Ukr. J. Low Temp. Phys. 28 510
[32] Windt M et al 2001 Phys. Rev. Lett. 87 127002
[33] Pisans I and Valentí R 2005 Preprint cond-mat/0501685
[34] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[35] Anisimov V, Aryasetiawan F and Lichtenstein A I 1997 J. Phys.: Condens. Matter 9 767
[36] Andersen O K 1975 Phys. Rev. Lett. 12 3060
[37] Andersen O K and Saha-Dasgupta T 2000 Phys. Rev. B 62 R16219, and references therein

New Journal of Physics 7 (2005) 74 (http://www.njp.org/)