PHYSICAL REVIEW B **81**, 125133 (2010)

Anisotropic crystal field, Mott gap, and interband excitations in TiOCl: An electron energy-loss study

Roberto Kraus, Bernd Büchner, and Martin Knupfer
IFW Dresden, Postfach 270116, D-01171 Dresden, Germany

Sebastian Glawion, Michael Sing, and Ralph Claessen
Experimentelle Physik 4, Universität Würzburg, D-97074 Würzburg, Germany

(Received 25 November 2009; revised manuscript received 25 February 2010; published 31 March 2010)

We have studied the quasi-one-dimensional Mott insulator TiOCl using electron energy-loss spectroscopy in transmission in a wide energy range. The measured loss function, $\mathrm{Im}(\frac{-1}{\epsilon(\mathbf{q},\omega)})$, of TiOCl reveals local, Ti 3*d* crystal field excitations, excitations across the Mott gap, and interband transitions, which all are significantly anisotropic. Momentum dependent investigations demonstrate that the excitations above the Mott gap are rather localized and they allow to identify the energetically highest, optically forbidden crystal field excitation. Performing a Kramers-Kronig analysis of the measured loss function we have derived the real and imaginary part of the dielectric function.

DOI: 10.1103/PhysRevB.81.125133 PACS number(s): 79.20.Uv, 71.27.+a, 78.20.−e, 71.70.Ch

I. INTRODUCTION

TiOCl as a quasi-one-dimensional Mott insulator with strong electronic correlations and as a compound with antiferromagnetic spin-1/2 Heisenberg chains has attracted a lot of interest in the last years. The system is one of the few inorganic spin-Peierls compounds[1] besides $CuGeO_3$ (Ref. 2) and NaV_2O_5.[3] The nonmagnetic ground state is formed by $S=0$ dimers in the chain, originated by a coupling with the lattice. The phase transition in TiOCl is unconventional and divided into two steps. Before the spin-Peierls state below 67 K is reached, first an incommensurate state below 91 K is passed,[4–6] which is possibly caused by interchain coupling and frustration.

TiOCl crystallizes in an orthorhombic layered structure where buckled Ti-O bilayers are separated by Cl ions. The interaction between the bilayers is of van der Waals type and thus rather weak. Locally, the Ti ions are coordinated by four O and two Cl ions, which form a distorted octahedral-like environment. Electronically, the system is characterized by one 3*d* electron per titanium site, and the interaction between adjacent Ti ions is substantially anisotropic giving rise to a quasi-one-dimensional electronic behavior. As a consequence, at room temperature TiOCl can be well described in terms of a spin-1/2 Heisenberg chain along the crystal *b* axis. The titanium states are well separated (by 2 eV) from the ligand oxygen and chlorine states and the hybridization between them is small.[7] Moreover, the orbital degeneracy of the 3*d* levels is completely lifted by the crystal field and the single *d* electron of the titanium occupies the y^2-z^2 orbital[8] (we denote the orbitals with x,y,z parallel to the crystal axes a,b,c, respectively).

Thus, TiOCl can be regarded as an archetype Mott insulator, which allows to study the electronic properties of such systems with various techniques. For instance, recent measurements using angular resolved photoemission spectroscopy have confirmed the quasi-one-dimensional character of the electronic bands[9] and investigations as a function of charge carrier doping[10,11] or upon the application of high pressure[12,13] have been carried out in order to probe a potential metal-insulator transition. The electronic excitations have been studied using optical techniques which have revealed insight into the low-energy excitations below the fundamental Mott gap. In this contribution we present an investigation of the electronic excitations of TiOCl using electron energy-loss spectroscopy (EELS) in transmission. With this method a broader energy range above the Mott gap is accessible and also measurements with a finite momentum transfer away from the optical limit are realizable. Our studies demonstrate the strong anisotropy of the crystal field excitations as well as of the transitions across the Mott gap and show that the dispersion of these excitations is negligible, which demonstrates their localized character. For the latter, this has to be contrasted with the corresponding excitations across the charge transfer gap in correlated cuprate based materials,[14,15] to reveal differences or similarities between charge transfer and Mott insulators.

II. EXPERIMENTAL

Single crystals of TiOCl have been grown using chemical vapor transport as described elsewhere.[16] For our EELS studies, thin, single-crystalline films with a thickness of approximately 100 nm are necessary and have been prepared by successive cleaving of a single crystal with adhesive tape. Since the system is layered and the bilayers are only weakly bounded by van der Waals forces perpendicular to the *c* direction, this procedure provides large enough, high quality films for our studies. These 100 nm thin films were then detached from the tape in acetone and mounted onto standard transmission electron microscopy grids. The quality of the films was checked *in situ* with electron diffraction, which demonstrated the single-crystalline structure of the films with the width of the Bragg peaks being limited by the instrumental resolution. Also no damage to the film was visible through prolonged exposure by the electron beam.

We performed EELS in transmission with a dedicated spectrometer which is described in more detail in Ref. 17.

1098-0121/2010/81(12)/125133(4)

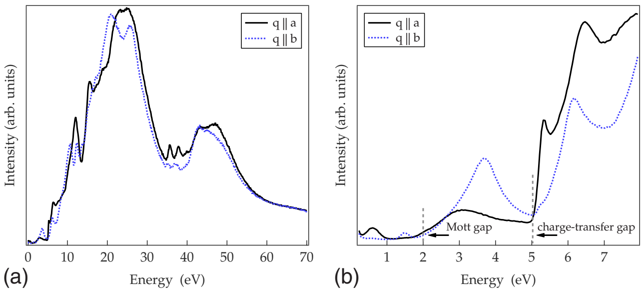

FIG. 1. (Color online) Loss function of TiOCl for a small momentum transfer of 0.1 Å^{-1} along the *a* and *b* crystal directions.

The primary beam energy was 172 keV, the energy and momentum resolution have been chosen to be 80 meV and 0.04 Å^{-1}, respectively. Note that at such a high primary beam energy only singlet excitations are possible,[17] due to negligible exchange interaction between electrons from the beam and the sample. EELS directly determines the loss function $\mathrm{Im}(\frac{-1}{\varepsilon(\mathbf{q},\omega)})$ as a function of energy and momentum, where $\varepsilon(\mathbf{q},\omega)$ denotes the complex dielectric function. Momentum dependent EELS studies provide access to, for instance, optically forbidden excitations[14,18] or the dispersion[19,20] of excitations. In addition, the spectrometer is equipped with a flow-cryostat allowing for temperature-dependent measurements with a minimum sample temperature of about 15 K. All measurements have been carried out at room temperature and 15 K, and the results are virtually identical. In the following, we therefore show the room temperature data only. For the Kramers-Kronig analysis the measured loss function has been corrected for the contributions from the elastic line.[17]

III. RESULTS AND DISCUSSION

Figure 1 shows the loss function of TiOCl for a small momentum transfer, q, of 0.1 Å^{-1} parallel to the *a* and *b* crystal axes. At such a small absolute value of momentum transfer, the data represent the optical limit and are thus equivalent to those from optical techniques.[17] The loss function is anisotropic throughout the energy range shown in Fig. 1 which is in correspondence to the anisotropic electronic structure of TiOCl. Several spectral structures are visible which are related to various interband excitations, the excitation of the volume plasmon in TiOCl (around 22 eV), a collective excitation of all valence electrons and also the Ti $M_{2,3}$ excitation edge at energies higher than 35 eV. The right panel of Fig. 1 focuses on the low-energy region and reveals that also the excitations in which the Ti 3*d* levels are involved are considerably anisotropic. At 0.6 eV for a momentum transfer parallel to the *a* axis and at 1.49 eV for $q \| b$, two features are observed which stem from (anisotropic) crystal field excitations within the Ti 3*d* states. These have also been observed using optical techniques,[5,21] and their character has been analyzed with cluster[8] or LDA+U calculations.[13] Accordingly, the feature at about 0.60 eV for $q \| a$ is ascribed to excitations from the $3d_{y^2-z^2}$ into $3d_{xz}$ orbitals while the loss feature at about 1.49 eV ($q \| b$) is due to $3d_{y^2-z^2} \rightarrow 3d_{yz}$ excitations. At 15 K in the spin-Peierls phase both crystal field excitations shift slightly to higher energy, 0.65 eV for $q \| a$ and 1.53 eV for $q \| b$.

Going to higher energies a relatively broad structure can be observed around 3–4 eV, which has a spectral onset at about 2 eV. At these energies, nonlocal excitations between neighboring Ti sites are expected, which reflect the anisotropic band structure as well as the local crystal field splitting and electronic correlations. For energies of 2–3 eV, the spectral weight in the loss function starts rather isotropic, but the two curves significantly differ at higher energies, where for a momentum transfer parallel *b* a clear maximum at about 3.7 eV is seen. In a multiorbital Hubbard model for a $3d^1$ system one can expect *d*-*d* intersite transitions at the energies $U-3J_H$, $U-J_H$, and $U+2J_H$,[22,23] with U as intraorbital Coulomb interaction and J_H as onsite exchange coupling. For titanium a value for U of 4.5 eV and J_H of 0.7 eV is reasonable.[24,25] The final state for electrons in different orbitals is characterized in the triplet state by an energy of $U-3J_H$ and in the singlet state by $U-3J_H$ and $U-J_H$. Taking into account the additional crystal field splitting, with values of 0.6 and 1.5 eV (see section above) and 0.3 and 2.1 eV, which are predicted by cluster calculations,[8] one obtains transition energies in the range of 2.7 to 5.9 eV. These excitations are in good agreement with the energy position of the broad structure as seen for $q \| a$. The final state with both electrons in the $3d_{y^2-z^2}$ orbital lies at $U-J_H$ and $U+2J_H$, which results in an energy value of 3.8 and 5.9 eV. These excitations are strongly anisotropic due to the direct overlap of the $3d_{y^2-z^2}$ orbitals along the crystallographic *b* direction giving rise to the quasi-one-dimensional character of the band structure. From investigations using angular resolved photoemission spectroscopy (ARPES) (Ref. 9) and from calculations[7] it is known that the conduction band width along the crystal *b* direction is about 0.5 eV and substantially larger than in the other directions. Therefore, also the spectral weight is expected to be much larger for a momentum transfer parallel to *b*. Finally this results in additional spectral weight for $q \| b$ giving rise to the pronounced maximum at 3.7 eV. The second peak at approx. 6 eV can not been seen clearly because it overlaps with charge transfer excitations.

Above 5 eV further sharp excitations can be observed in Fig. 1. These arise from charge-transfer excitations from occupied oxygen or chlorine derived states into the titanium 3*d* states. The energy, where the steep threshold appears in the loss function, is in good agreement to the binding energy of 4.5 eV[9] of these states as seen by photoemission spectroscopy or predicted by band structure calculations[26] plus the half charge gap of 1 eV. Also here, the anisotropic nature of the TiOCl electronic properties is reflected.

Momentum dependent studies of the loss function as shown in Fig. 2 complement our knowledge on the excitations in TiOCl. The low energy, local crystal field excitations (at 0.6 and 1.5 eV, respectively) decrease in intensity with increasing momentum transfer, which is a direct consequence of their dipole allowed character.[18] Moreover, they do not change in energy upon variation in momentum in correspondence to their localized character. For a momentum transfer parallel to *a* a further excitation feature appears at about 2.1 eV at higher momentum transfers (see inset in the

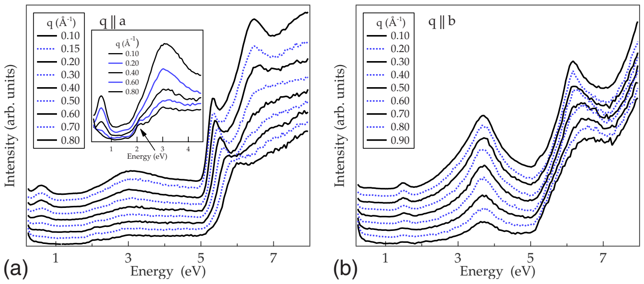

FIG. 2. (Color online) Momentum dependence of the loss function of TiOCl along the *a* and *b* crystal directions. No dispersion is visible for the crystal field and Mott gap excitations. The higher lying charge transfer excitations ($E > 5$ eV) show a clear dispersion. The inset in the left panel for $\mathbf{q} \parallel a$ shows the appearance of an optically forbidden crystal field excitation at 2.1 eV.

left panel of Fig. 2). This is reminiscent of the behavior of optically forbidden excitations,[14,27] and we associate this 2.1 eV feature with crystal field excitations into the highest crystal field level, which have not been experimentally identified so far. Our assignment is in good agreement with previous cluster calculations,[8] which predicted this excitation at this energy with a polarization along the *c* axis. Therefore, this excitation is not accessible with optical spectroscopy methods because this polarization corresponds to the stacking direction of the layered crystal structure with a limited thickness in the single crystals of 0.1 mm. For the lowest optical forbidden crystal field excitation expected at approximately 0.3 eV no predication is possible because of the intersection with the elastic line.

For the nonlocal excitations between 2 and 5 eV, we also observe no energy shift and a decreasing spectral weight upon increasing momentum transfer, i.e., also these excitations are rather localized and of predominant dipole allowed character. In contrast, the charge transfer excitations at higher energies clearly disperse. It is not surprising that the nonlocal crystal field excitations do not show a dispersion since the overlap of the associated orbitals is small. In case of the excitation across the Mott gap as seen at 3.7 eV in the right panel of Fig. 2, the localized character cannot be explained on the basis of a band-structure picture. There, these excitations should have a bandwidth similar to the involved single particle bands,[17] which is about 0.5 eV.[9,26] On the other hand, it is not clear at present to what extend the excitation across the Mott gap is of excitonic nature which would naturally also change its momentum behavior. For instance, within an extended Hubbard model taking into account a next-nearest Coulomb interaction *V*, the formation of excitons and a change in dispersion could be rationalized.[20,28] Furthermore, these excitations might also couple to further degrees of freedom, e.g., phonons, which would cause an increase in the effective mass, i.e., a decrease in the associated dispersion. In earlier EELS studies of cuprate systems,[15,20] which are charge-transfer insulators, a sizable dispersion of the excitations across the charge transfer gap has been observed, which indeed scales with the charge carrier hopping parameters of the involved single particle bands, as for instance given in a tight-binding description.[29]

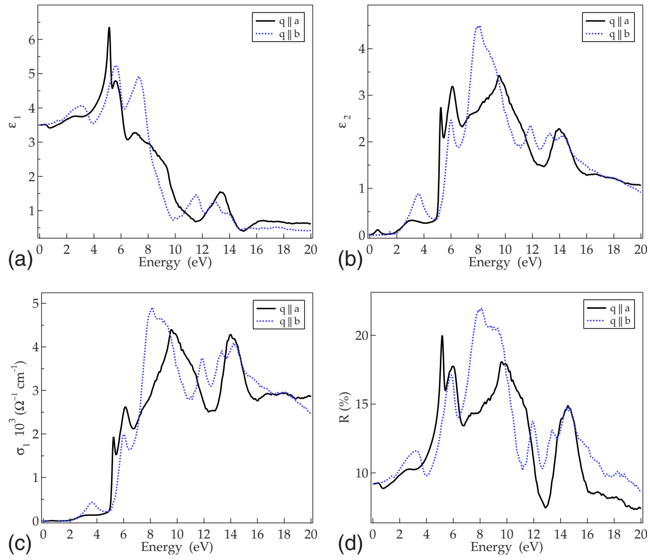

FIG. 3. (Color online) ε_1 and ε_2 of TiOCl derived by a Kramers-Kronig analysis of the loss functions. Additionally the optical conductivity σ_1 and the reflectivity *R* is depicted.

For the charge transfer excitations above 5 eV a clear positive dispersion and broadening is visible, indicating a rather delocalized character. This is consistent with ARPES measurements, where a clear dispersion was also seen for the occupied oxygen and chlorine states.[9] The shape of the dispersion is roughly proportional to $q^{1.6}$ for both polarization directions.

Finally, we have performed a Kramers-Kronig analysis of the measured loss function in order to calculate the real and imaginary part of the complex dielectric function at a momentum transfer of 0.1 Å^{-1} (optical limit). The normalization during this procedure has been achieved via a comparison with the available reflectivity data. With a value for the static dielectric constant $\epsilon(\omega=0)$ of 3.5 we obtain the best agreement with experimental data from earlier reflectivity measurements.[30,31] In Fig. 3 we present the results of our Kramers-Kronig analysis for the real part ε_1 and the imaginary part ε_2 of the dielectric function and in addition the optical conductivity $\sigma_1 = \omega \varepsilon_2$ and the reflectivity *R*. These data complement in a much larger energy window what is known on the optical response of TiOCl so far. The excitations discussed in the previous paragraphs can also be seen in these response functions, respectively, and also the anisotropy of the dielectric response of TiOCl is reflected in the curves in Fig. 3.

IV. SUMMARY

In summary, we have studied the system TiOCl with EELS in transmission. Our data show the strongly anisotropic nature of the electronic excitations in this archetype Mott insulator. We have observed crystal field excitations within the Ti 3*d* orbitals and our data allow to determine the energy of the highest lying crystal field excitation at 2.1 eV which was experimentally unidentified so far. Both the crystal field excitation and the excitation across the Mott gap show negligible dispersion, i.e., they are rather localized. A Kramers-Kronig analysis of the measured loss functions provided the anisotropic dielectric function, from which other optical functions can be calculated.

ACKNOWLEDGMENTS

We thank A. M. Oleś and R. Valentí for fruitful discussions, T. Demarczyk for the crystal growth, and R. Hübel, S. Leger, and R. Schönfelder for technical assistance. The project was funded by DFG under Grant No. CL 124/6-1.

---

[1] A. Seidel, C. A. Marianetti, F. C. Chou, G. Ceder, and P. A. Lee, Phys. Rev. B **67**, 020405(R) (2003).

[2] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993).

[3] M. Isobe and Y. Ueda, J. Phys. Soc. Jpn. **65**, 1178 (1996).

[4] A. Krimmel, J. Strempfer, B. Bohnenbuck, B. Keimer, M. Hoinkis, M. Klemm, S. Horn, A. Loidl, M. Sing, R. Claessen, and M. v. Zimmermann, Phys. Rev. B **73**, 172413 (2006).

[5] R. Rückamp, J. Baier, M. Kriener, M. W. Haverkort, T. Lorenz, G. S. Uhrig, L. Jongen, A. Möller, G. Meyer, and M. Grüninger, Phys. Rev. Lett. **95**, 097203 (2005).

[6] Y.-Z. Zhang, H. O. Jeschke, and R. Valentí, Phys. Rev. B **78**, 205104 (2008).

[7] T. Saha-Dasgupta, R. Valentí, H. Rosner, and C. Gros, Europhys. Lett. **67**, 63 (2004).

[8] R. Rückamp, E. Benckiser, M. W. Haverkort, H. Roth, T. Lorenz, A. Freimuth, L. Jongen, A. Möller, G. Meyer, P. Reutler, B. Büchner, A. Revcolevschi, S.-W. Cheong, C. Sekar, G. Krabbes, and M. Grüninger, New J. Phys. **7**, 144 (2005).

[9] M. Hoinkis, M. Sing, J. Schäfer, M. Klemm, S. Horn, H. Benthien, E. Jeckelmann, T. Saha-Dasgupta, L. Pisani, R. Valentí, and R. Claessen, Phys. Rev. B **72**, 125127 (2005).

[10] M. Sing, S. Glawion, M. Schlachter, M. R. Scholz, K. Goß, J. Heidler, and R. Claessen, arXiv:0905.1381 (unpublished).

[11] Y.-Z. Zhang, K. Foyevtsova, H. O. Jeschke, M. U. Schmidt, and R. Valentí, arXiv:0905.1276 (unpublished).

[12] C. A. Kuntscher, S. Frank, A. Pashkin, H. Hoffmann, A. Schönleber, S. van Smaalen, M. Hanfland, S. Glawion, M. Klemm, M. Sing, S. Horn, and R. Claessen, Phys. Rev. B **76**, 241101(R) (2007).

[13] Y.-Z. Zhang, H. O. Jeschke, and R. Valentí, Phys. Rev. Lett. **101**, 136406 (2008).

[14] S. Atzkern, M. Knupfer, M. S. Golden, J. Fink, C. Waidacher, J. Richter, K. W. Becker, N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. B **62**, 7845 (2000).

[15] J. Fink, M. Knupfer, S. Atzkern, and M. S. Golden, J. Electron Spectrosc. Relat. Phenom. **117-118**, 287 (2001).

[16] H. Schäfer, F. Wartenpfuhl, and E. Weise, Z. Anorg. Allg. Chem. **295**, 268 (1958).

[17] J. Fink, Adv. Electron. Electron Phys. **75**, 121 (1989).

[18] M. Knupfer, J. Fink, E. Zojer, G. Leising, and D. Fichou, Chem. Phys. Lett. **318**, 585 (2000).

[19] R. Schuster, M. Knupfer, and H. Berger, Phys. Rev. Lett. **98**, 037402 (2007).

[20] R. Neudert, M. Knupfer, M. S. Golden, J. Fink, W. Stephan, K. Penc, N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. Lett. **81**, 657 (1998).

[21] C. A. Kuntscher, S. Frank, A. Pashkin, M. Hoinkis, M. Klemm, M. Sing, S. Horn, and R. Claessen, Phys. Rev. B **74**, 184402 (2006).

[22] J. S. Lee, M. W. Kim, and T. W. Noh, New J. Phys. **7**, 147 (2005).

[23] A. M. Oleś, G. Khaliullin, P. Horsch, and L. F. Feiner, Phys. Rev. B **72**, 214431 (2005).

[24] A. E. Bocquet, T. Mizokawa, K. Morikawa, A. Fujimori, S. R. Barman, K. Maiti, D. D. Sarma, Y. Tokura, and M. Onoda, Phys. Rev. B **53**, 1161 (1996).

[25] T. Mizokawa and A. Fujimori, Phys. Rev. B **54**, 5368 (1996).

[26] M. Hoinkis, M. Sing, S. Glawion, L. Pisani, R. Valentí, S. van Smaalen, M. Klemm, S. Horn, and R. Claessen, Phys. Rev. B **75**, 245124 (2007).

[27] M. Knupfer and J. Fink, Phys. Rev. B **60**, 10731 (1999).

[28] M. B. J. Meinders, J. van den Brink, J. Lorenzana, and G. A. Sawatzky, Phys. Rev. B **52**, 2484 (1995).

[29] F. C. Zhang and K. K. Ng, Phys. Rev. B **58**, 13520 (1998).

[30] G. Caimi, L. Degiorgi, N. N. Kovaleva, P. Lemmens, and F. C. Chou, Phys. Rev. B **69**, 125108 (2004).

[31] P. Lemmens, K. Y. Choi, G. Caimi, L. Degiorgi, N. N. Kovaleva, A. Seidel, and F. C. Chou, Phys. Rev. B **70**, 134429 (2004).