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Pressure-induced metallization and structural phase transition of the Mott-Hubbard insulator TiOBr

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We investigated the pressure-dependent optical response of the low-dimensional Mott-Hubbard insulator TiOBr by transmittance and reflectance measurements in the infrared and visible frequency range. A suppression of the transmittance above a critical pressure and a concomitant increase of the reflectance are observed, suggesting a pressure-induced metallization of TiOBr. The metallic phase of TiOBr at high pressure is confirmed by the presence of additional excitations extending down to the far-infrared range. The pressure-induced metallization coincides with a structural phase transition, according to the results of x-ray powder diffraction experiments under pressure.

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The titanium oxyhalides Ti*OX*, with X=Cl or Br, are spin-Peierls compounds with exotic properties.[1–7] The magnetic properties are related to the direct exchange interaction between the spins on different Ti ions along the crystal axis b, forming an antiferromagnetic, one-dimensional spin-1/2 Heisenberg chain. With the electronic configuration $3d^1$ these materials are Mott-Hubbard insulators with a charge gap of $\approx$2 eV.[3,8,9] They have been earlier discussed to exhibit a resonating valence bond state and high-temperature superconductivity upon doping.[10,11] However, up to now a metallization of Ti*OX* upon doping was not successful.[12]

Recent pressure-dependent infrared spectroscopic investigations on TiOCl suggest that the application of external pressure is an alternative way to induce an insulator-to-metal transition in Ti*OX*:[9] Above 12 GPa the infrared transmittance is suppressed and the reflectance abruptly increases. Concomitantly, the sample color changes. From the pressure dependence of the absorption edge the closure of the charge gap at around 12 GPa was inferred. The pressure-induced changes were attributed to the onset of additional excitations in the infrared frequency range, suggesting an insulator-to-metal transition. However, the metallization of TiOCl could not be directly proved, since the spectroscopic studies were restricted to the near-infrared range. Furthermore, due to the lack of pressure-dependent crystal structure data it could not be decided whether the presumable insulator-to-metal transition is bandwidth-controlled, i.e., whether it is of pure electronic origin and can be described in the frame of the Mott transition,[13,14] or whether additionally changes in the crystal symmetry have to be considered.

To address these open issues, we have extended our pressure studies in several respects: (i) extension of the spectroscopic investigations to the far-infrared range, in order to verify the pressure-induced metallization; (ii) x-ray diffraction measurements under pressure, in order to clarify the origin of the observed pressure dependence of the optical response. Furthermore, we have carried out corresponding studies on the analog TiOBr.

For TiOCl and TiOBr we found consistent spectroscopic results, namely evidence for the metallization of the materials under pressure. Furthermore, the metallization coincides with a structural phase transition induced by external pressure. In this paper we focus on the material TiOBr. An extensive and comparative presentation of all our results for both compounds TiOBr and TiOCl will be presented in a forthcoming paper.[21]

Single crystals of TiOBr were synthesized by the chemical vapor transport technique. TiOBr crystallizes in the space group *Pmmn* consisting of buckled Ti-O bilayers parallel to the *ab* plane and separated by layers of Br ions stacked along the *c* direction.[15]

In our pressure-dependent studies diamond anvil cells (DACs) were used for the generation of pressures. The applied pressures were determined with the ruby luminescence method.[16] For the transmittance measurements argon was used as the pressure medium. For the reflectance measurements finely ground CsI powder was chosen as the pressure medium to ensure direct contact of the sample with the diamond window. For each transmittance and reflectance measurement a small piece (about 80 μm $\times$ 80 μm) was cut from single crystals with a thickness of $\leqslant$5 μm and placed in the hole of a steel gasket.

Pressure-dependent transmittance and reflectance experiments were conducted at room temperature using a Bruker IFS 66v/S FT-IR spectrometer with an infrared microscope (Bruker IRscope II). Part of the measurements were carried out at the infrared beamline of the synchrotron radiation source ANKA, where the same equipment is installed. The reproducibility of the results was ensured by several experimental runs on different pieces of crystals. The geometries for the transmittance and reflectance measurements are the same as used in Ref. 9. The pressure-dependent transmittance was studied in the frequency range 2400–22 000 cm^{-1} (0.30–2.7 eV) for the polarization directions $\mathbf{E}\|a,b$. We measured the intensity $\mathbf{I}_s(\omega)$ of the radiation transmitted by the sample; as a reference, for each pressure we focused the

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incident radiation spot on the empty space in the gasket hole next to the sample and obtained the transmitted intensity $\mathbf{I}_r(\omega)$. The ratio $T(\omega)=\mathbf{I}_s(\omega)/\mathbf{I}_r(\omega)$ is a measure of the transmittance of the sample.

Pressure-dependent reflectance measurements were carried out in the frequency range $\approx 250-7500\ \text{cm}^{-1}$ (0.03–0.93 eV) for $\mathbf{E}\|a,b$. Reflectance spectra $R_{s\text{-}d}$ of the sample with respect to diamond were obtained by measuring the intensity $I_{s\text{-dia}}(\omega)$ reflected at the interface between the sample and the diamond anvil.[9] As a reference, the intensity $I_{\text{dia}}(\omega)$ reflected from the inner diamond-air interface of the empty DAC was used. The reflectance spectra were calculated according to $R_{s\text{-}d}(\omega)=R_{\text{dia}}I_{s\text{-dia}}(\omega)/I_{\text{dia}}(\omega)$, where R_{dia} was estimated from the refractive index of diamond n_{dia} to 0.167 and assumed to be independent of pressure.[17,18]

Pressure-dependent x-ray powder diffraction measurements at room temperature were carried out with monochromatic radiation ($\lambda=0.4128$ Å) at beamline ID09A of the European Synchrotron Radiation Facility at Grenoble. Crystals were ground and placed into a DAC for pressure generation. Helium served as hydrostatic pressure-transmitting medium. Diffraction patterns were recorded with an image plate detector and then integrated[19] to yield an intensity vs 2θ diagrams. The DAC was rotated by ±3° during the exposure to improve the powder averaging. We carried out LeBail fits of the diffraction data using the JANA2000 software,[20] in order to determine the lattice parameters as a function of pressure. The analysis of the x-ray diffraction data is, however, complicated by the preferred orientation of the crystallites inside the DAC, with the c crystal axis oriented perpendicular to the diamond anvil surface, i.e., along the direction of incidence of the x-radiation. Therefore, Rietveld refinements of the diffraction patterns could not be carried out.

In Fig. 1 we present the room-temperature transmittance spectra of TiOBr as a function of pressure for the polarizations $\mathbf{E}\|a,b$. The optical response of TiOBr resembles that of TiOCl:[9] For the lowest applied pressure the transmittance is suppressed above ≈ 2 eV due to excitations across the charge gap. The absorption at $5060\ \text{cm}^{-1}$ (0.63 eV) for $\mathbf{E}\|a$ and at $10\,950\ \text{cm}^{-1}$ (1.35 eV) for $\mathbf{E}\|b$ are due to excitations between the crystal field-split Ti $3d$ energy levels.[3,8] These excitations are infrared active due to the lack of inversion symmetry on the Ti sites; they are slightly shifted in energy compared to TiOCl (for TiOCl the energies are 0.66 and 1.53 eV for $\mathbf{E}\|a$ and $\mathbf{E}\|b$, respectively).[9] The experimental values are in agreement with recent cluster calculations,[7] where corresponding crystal field splittings of $3d^1$ Ti^{3+} with approximate size 0.66–0.68 eV (0.65–0.67 eV) and 1.59–1.68 eV (1.48–1.43 eV) for TiOCl (TiOBr) were obtained.

The pressure-induced changes (see Fig. 1) are similar to those found for TiOCl:[9] With increasing pressure the orbital excitations broaden and continuously shift to higher frequencies. The absorption edge due to the excitations across the charge gap shifts to lower energies, and above ≈ 14 GPa the $\mathbf{E}\|a,b$ transmittance is suppressed over the whole studied frequency range. As for TiOCl, a change of the sample color from red to black occurs upon pressure increase (not shown). A quantitative presentation of the pressure dependence of the orbital excitations and the charge gap in TiOBr will be given in a forthcoming paper.[21]

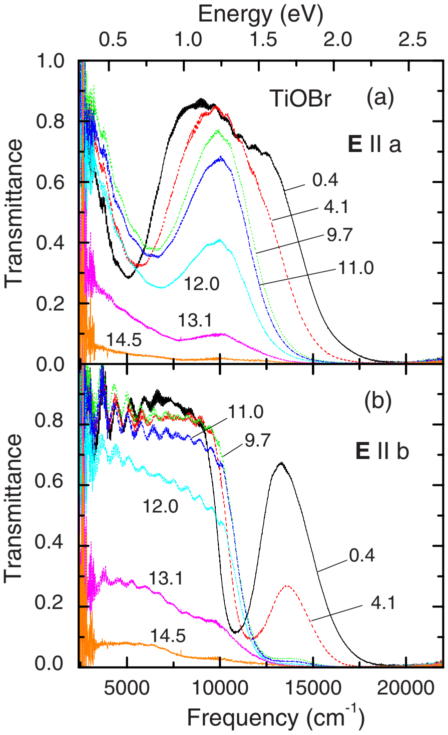

FIG. 1. (Color online) Room-temperature transmittance $T(\omega)=\mathbf{I}_s(\omega)/\mathbf{I}_r(\omega)$ (see text for definitions) of TiOBr as a function of pressure for the polarization (a) $\mathbf{E}\|a$ and (b) $\mathbf{E}\|b$ (pressure medium: argon). The numbers indicate the applied pressures in GPa.

Reflectance spectra measured at low pressures do not provide information about the reflectivity of TiOBr, because at low pressures the thin TiOBr crystal in the DAC is partially transparent in the infrared range (see Fig. 1), and interference fringes occur in the reflectance spectra due to multiple reflections within the sample (data not shown). On increasing pressure the interference fringes diminish and they have disappeared above $P=10$ GPa, at which pressure $R_{s\text{-}d}(\omega)$ abruptly increases in the whole studied frequency range (far infrared to near infrared), for both polarization directions. The reflectance spectra $R_{s\text{-}d}(\omega)$ in the high-pressure (>10 GPa) regime are shown in Fig. 2. The difference in the critical pressure P_{cr} derived from the transmittance ($P_{\text{cr}}=14$ GPa) and reflectance ($P_{\text{cr}}=10-11$ GPa) measurements are due to the different pressure media used.[9,22] The observation of an enhanced reflectance of TiOBr in the infrared range above ≈ 10 GPa is consistent with our earlier results for TiOCl.[9] However, for TiOCl this enhancement occurs at slightly higher (12 GPa) pressure,[23] indicating that TiOBr is more sensitive to the application of pressure. This is also suggested by the pronounced pressure-induced changes in the transmittance spectra of TiOBr (see Fig. 1) occurring already in the low-pressure regime.

Following the data analysis applied in Ref. 9, we fitted the reflectance spectra with the Drude-Lorentz model to obtain

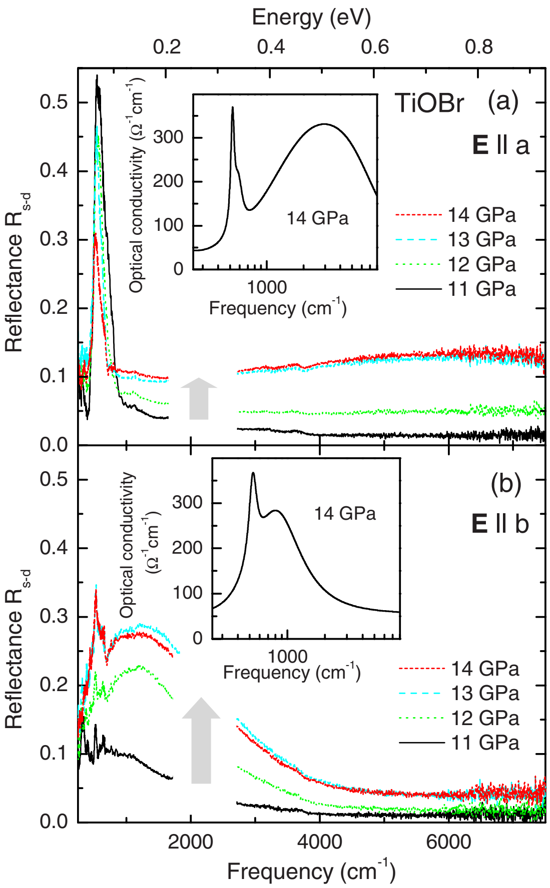

FIG. 2. (Color online) Room-temperature reflectance spectra $R_{s\text{-}d}(\omega)$ of TiOBr as a function of pressure for the polarization (a) $\mathbf{E}\|a$ and (b) $\mathbf{E}\|b$ (pressure medium: CsI). Arrows indicate the changes with increasing pressure. Insets: Real part of the optical conductivity spectra of TiOBr at the highest pressure (14 GPa) obtained by fitting the reflectance spectra $R_{s\text{-}d}(\omega)$ with the Drude-Lorentz model.

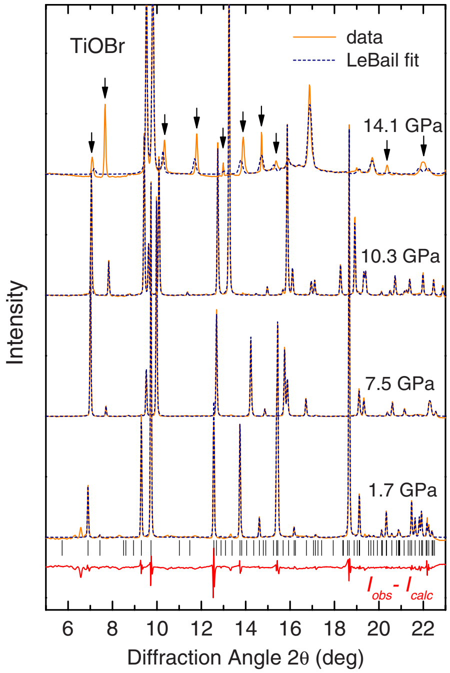

FIG. 3. (Color online) Room-temperature x-ray powder diffraction diagrams of TiOBr at high pressures ($\lambda = 0.4128$ Å) together with the LeBail fits (pressure medium: helium). For the lowest applied pressure (1.7 GPa) the difference curve ($I_{\text{obs}} - I_{\text{calc}}$) between the diffraction diagram and the LeBail fit is shown. Markers show the calculated peak positions for the ambient-pressure phase. Above 14 GPa the diffraction diagram can no longer be described by the ambient-pressure crystal symmetry. Arrows indicate the diffraction peaks with the most obvious discrepancy between the data and the LeBail fitting curve.

information about the pressure-induced excitations. The real part of the optical conductivity of TiOBr at 14 GPa is presented in the insets of Fig. 2 for the polarizations $\mathbf{E}\|a,b$. At high pressure additional excitations occur, which extend down to the far-infrared range. This finding indicates the metallization of the sample under pressure.

Two scenarios were discussed[9] to explain the observed pressure-induced excitations inside the Mott-Hubbard gap of TiOCl: a bandwidth-controlled insulator-to-metal transition, i.e., a Mott transition of purely electronic character,[13,14] and a structural phase transition entering a metallic phase. To clarify this issue, we carried out x-ray powder diffraction experiments as a function of pressure. Figure 3 shows the room-temperature diffraction diagrams of TiOBr for selected pressures together with the LeBail fits. Obviously, at low pressure the diffraction diagram can be well fitted with the ambient-pressure crystal structure (space group *Pmmn*). We could therefore obtain the lattice parameters and unit cell volume as a function of pressure.[21] The most important finding, however, is that the diffraction diagram undergoes pronounced changes at around 14 GPa and is no longer compatible with the ambient-pressure crystal structure symmetry. These drastic changes in the diffraction data related to a structural phase transition coincide with the changes in the optical properties described above. Corresponding results are found for the analog compound TiOCl.[21] This points out that for a proper description of the pressure-induced transition in TiOBr and TiOCl the lattice degree of freedom has to be taken into account besides correlation effects in the electronic subsystem.

In conclusion, we studied the pressure dependence of the polarization-dependent optical response of the low-dimensional Mott-Hubbard insulater TiOBr in the infrared and visible frequency range at room temperature. The most interesting effects induced by pressure are the suppression of the transmittance and the increase in the reflectance above a critical pressure, suggesting the occurrence of an insulator-to-metal transition. The metallization of TiOBr at high pressure is evidenced by the finite optical conductivity in the far-infrared frequency range. According to our pressure-dependent x-ray powder diffraction results, the pressure-induced insulator-to-metal transition coincides with a structural phase transition for pressures around 14 GPa under hydrostatic conditions. Our finding of a metallic phase in TiOBr under pressure raises the question whether a superconducting state occurs in pressurized TiO*X* (*X*=Br,Cl) at low temperature.

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