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Small polaron characteristics of an OD center in TiO_2 studied by infrared spectroscopy

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Abstract

The fundamental OD center in TiO_2 has been studied by infrared absorption spectroscopy and by theory. Our experiments reveal a single sharp OD line in oxygenated samples that we attribute to a positively charged center. In TiO_2 samples reduced by a treatment in a D_2 ambient at 500 °C, a neutral OD center with two additional IR lines is produced. Similar results reported recently by Herklotz *et al.* [Phys. Rev. B **83**, 235202 (2011)] led them to suggest that the neutral OD center is a shallow donor with IR lines arising from its two charge states. Our analysis suggests instead that the properties of the neutral OD center are explained by a small polaron model which involves several configurations corresponding to the localization of the electron on different nearby Ti sites.

I. Introduction

The properties of interstitial H (H_i) in rutile TiO_2 have been studied over many years, and several significant results have emerged: (1) H_i attaches to a single lattice O such that the O-H bond lies perpendicular to the c axis of the rutile lattice.^{1,2} (2) H_i diffuses readily along the large interstitial channel in the c-direction, which makes its existence at room temperature puzzling.³⁻⁵ (3) OH and its isotopic siblings OD and OT exhibit strong fundamental stretch modes with unusually large anharmonicity.⁶

Furthermore, recent EPR experiments on neutral H_i as well as on F substituting for O in mildly reduced TiO_2 show a characteristic that is unusual in most materials, especially semiconductors: the spin associated with the unpaired electron in each case is localized on a single Ti, rather than being spread out over many sites.^{7,8} Finally, while the classic vibrational spectra reported by Bates and Perkins⁶ show a single sharp line for each isotope (2445 cm^{-1} for OD), more recent results of Herklotz *et al.*⁹ reveal IR lines for OD at 2445.0 , 2445.7 , and 2447.8 cm^{-1} whose relative intensities are strongly dependent on temperature. Herklotz *et al.* have proposed that the OD center (and also OH) **is a shallow donor** and have assigned the multiline structure to its two different charge states. In addition, they found the changes in the intensities of these OD lines to be correlated with the temperature dependence of additional broad absorption that was attributed to free carriers¹⁰ introduced by the OD (or OH) shallow donor.

In order to address these and other significant questions concerning the nature of H_i in TiO_2 , we have carried out further experimental and theoretical studies. In the present work we focus on the OD center rather than OH because the IR lines for OD are sharper and reveal greater detail. We carry out high-resolution vibrational spectroscopy as a function of temperature to gain insight into the different vibrational properties seen for OD in TiO_2 in the 1970's and in recent studies and into how these results might be interpreted.

II. Experiment

Remarkably, in addition to samples from Commercial Crystal Laboratories, we have in our possession the very rutile TiO_2 samples, grown by the National Lead Co., that were studied by Bates and Perkins⁶ (BP) in the 1970's. These samples are disks, approximately 2 mm thick, with faces parallel to the (100) plane. BP deuterated their samples by heating a disk for 5 h in 0.4 atm of D_2 gas at 600 °C. These disks were subsequently heated for 2 h at 800 °C in flowing oxygen to restore their visible transparency.

TiO_2 crystals used in our experiments were deuterated by annealing in sealed quartz ampoules that contained 2/3 atm of D_2 gas. The treatment in D_2 was terminated by quenching the ampoule in water at room temperature. Any additional annealing treatments were performed in a tube furnace either in a flowing N_2 ambient or in air. IR absorption spectra were measured with a Bomem DA.3 Fourier transform infrared spectrometer equipped with an InSb detector. Light was polarized with a wire grid polarizer. An Oxford Instruments CF1204 cryostat with He contact gas was used for making temperature dependent measurements between 4 K and 60 K.

IR spectra are shown in Fig. 1(a) for TiO_2 samples taken from the collection that had been prepared by BP in the 1970's (and stored in dated sample boxes). The lower spectrum shows three partially resolved OD lines similar to the recent results of Herklotz *et al.*⁹ The upper spectrum shows a single sharp OD line at 2445.0 cm^{-1} similar to the results of BP.⁶

IR spectra are shown in Fig. 1(b) for TiO_2 samples that were prepared at Lehigh. The lower spectrum, measured for a sample treated in D_2 gas (at 500 °C for 4 h) and quenched to room temperature without any additional treatment, shows three partially resolved OD lines. This sample was made blue in color by the treatment in D_2 .¹¹ The upper spectrum, measured after a subsequent anneal in air (500 °C for 30 min), shows the single sharp IR line at 2445.0 cm^{-1} that was studied by BP. The anneal in air caused the blue color to disappear, restoring the sample's visible transparency. We obtained similar IR results for TiO_2 samples obtained from the collection of BP and from the Commercial Crystal Laboratories.

We focus first on the samples treated at Lehigh whose spectra are shown in Fig. 1(b). The sample treated in D₂ and then annealed in air shows an IR spectrum that is dominated by a single sharp IR line that can be attributed to a positively charged OD center [in ionic notation (ref. 12), O²⁻D⁺ or OD⁺] that is present in a more fully oxygenated sample. The sample treated in D₂ alone shows the two additional IR lines at 2445.7 and 2447.8 cm⁻¹ that can be attributed to the neutral OD center present in a reduced TiO₂ sample along with the line at 2445.0 cm⁻¹ that is due to OD⁻.

The results in Figs. 1(a) and 1(b) are remarkably similar. Deuterated samples studied by BP were annealed in flowing O₂ prior to IR measurements and show the line at 2445.0 cm⁻¹ due to the OD⁻ center.⁶ Our measurements show that not all of these samples were fully oxygenated and that samples also containing neutral OD centers can be found among the collection of BP. Many of their spectra were measured at 77 K. In this case, the multiple line structure could easily have been missed even if present because of the overlapping line shapes. Presumably, IR results reported for samples measured at 10 K by BP were for samples that had been fully oxygenated and the additional lines due to the neutral OD center were not detected. This resolves the puzzling discrepancy between the results of BP⁶ and those of Herklotz *et al.*⁹

We have measured the temperature dependence of the three partially resolved OD lines for a TiO₂ sample annealed in D₂. Representative spectra are shown in Fig. 2 (upper curves). We have also measured the temperature dependence for the 2445.0 cm⁻¹ line alone for a D₂-treated sample annealed subsequently also in air. The contribution of the 2445.0 cm⁻¹ line assigned to OD⁻ to the partially resolved OD lines, seen for a sample annealed in D₂ alone (upper spectra in Fig. 2), is found by our analysis of the line shapes to be constant for the temperature range we have examined (3.5 K to 60 K). This result has allowed us to subtract the contribution of the 2445.0 cm⁻¹ line, measured separately for the sample annealed in air, from spectra measured for reduced samples, temperature by temperature, to produce spectra for the neutral OD center alone (see center curves in each panel of Fig. 2). The spectra for the neutral OD center could then be fit by the sum of two Voigt line shapes (lower curves in each panel of Fig. 2) with frequencies (4 K) of $\omega_L=2445.7$ cm⁻¹ and $\omega_H=2447.8$ cm⁻¹.

The integrated areas of the two absorbance lines attributed to the neutral OD center [$A(\omega_L)$ and $A(\omega_H)$] have an interesting dependence on temperature. Between 4 and 20 K, $A(\omega_L)$ decreases while $A(\omega_H)$ increases, showing what appears to be a simple activated behavior. However, above 20 K, $A(\omega_L)$ regains intensity while $A(\omega_H)$ loses intensity. Fig. 3 shows the integrated areas $A(\omega_L)$ and $A(\omega_H)$ as a function of temperature. Fig. 4 shows a semi-log plot of the ratio of these areas, $A(\omega_H) / A(\omega_L)$, vs T^{-1} .

The temperature dependence of the IR lines cannot be fit by a simple model with two components with different energies. Herklotz *et al.* proposed a model with two components for the neutral OD center.⁹ Furthermore, at elevated temperature, neutral OD was proposed to become ionized to give an IR line near ω_L . A correlation of the ionization of neutral OD with the appearance of absorption attributed by Herklotz *et al.* to free carriers supported this suggested model. The overall conclusion of Herklotz *et al.*⁹ is that D (or H) gives rise to a shallow donor in TiO_2 with an ionization energy of 10 meV and Drude-like, free-carrier absorption.¹⁰

On the contrary, we favor a different model to explain the temperature dependence of the IR lines shown in Figs. 3 and 4. We have not observed any appreciable absorption in our spectra that might be associated with free carriers. This leads us to propose a model for the temperature dependence of the lines at ω_L and ω_H that involves the properties of the neutral OD center alone. We consider a model for neutral OD with at least three configurations with different energies (see the insets to Fig. 4). In this model, the neutral OD configuration with lowest energy, E_1 , gives a line at ω_L . The configuration with energy E_2 gives a line at ω_H . And the configuration with energy E_3 gives a line again at ω_L that is indistinguishable from the contribution from the configuration with energy E_1 . In this model, the area of the line at ω_L , for example, is given by the expression,

$$A(\omega_L) = [p_1 g_1 + p_3 g_3 \exp(-E_3/kT)]/Z. \quad (1)$$

Here, the g_i are the degeneracies of the different levels and the p_i account for the fact that the IR transitions for the different configurations can have different oscillator strengths. Z is the partition

function for the 3-level system shown in the inset to Fig. 4. The ratio of the areas of the IR lines at ω_L and ω_H shown in Fig. 4 is given by,

$$A(\omega_H)/A(\omega_L) = p_2 g_2 \exp(-E_2/kT) / [p_1 g_1 + p_3 g_3 \exp(-E_3/kT)]. \quad (2)$$

The slope of the curve in Fig. 4 at low temperature (<10 K) yields the energy $E_2 = 0.5$ meV. The slope of the curve in Fig. 4 at higher temperatures (>35 K) yields the energy $E_3 = 11$ meV. The y-intercepts for the curve shown in Fig. 4 provide relationships between the g_i and p_i parameters. Furthermore, these g_i and p_i parameters have been adjusted to provide the fit to the line intensities shown in Fig. 3. These fits show that the parameters p_i vary by only small factors near 1, consistent with the expectation that different OD configurations should have similar oscillator strengths. Our fits also show that the levels E_1 and E_2 have similar degeneracies of order one. However, the sharpness of the transition between ascending and descending slopes seen for $\log[A(\omega_H)/A(\omega_L)]$ vs T^{-1} in Fig. 4 requires a larger degeneracy for the level E_3 , that is, a value of $g_3 \approx 19$.

III. Small polaron model

What is the physical origin of the three configurations with different energies that explains the temperature dependence of our IR results? We have used the CRYSTAL06 code¹³ to investigate various properties of TiO_2 and H_i in this rutile lattice. We chose a hybrid DFT approach with a gradient-corrected approximation to the exchange-correlation functional [Becke's B3LYP potential¹⁴ with (in most cases) 20 % exact exchange and Lee-Yang-Parr correlation¹⁵]. The calculations were carried out in a periodic supercell with 48 or 72 host atoms, with computed lattice constants $a = 4.572$ Å, $c = 2.984$ Å, and $u = 0.305$. Gaussian basis functions¹⁶⁻¹⁸ were of the type 8411 for O, 8651(d3) for Ti, and 311p(1) for H.

TiO_2 has unusual electronic properties because the Ti d-like character of the lowest conduction bands¹⁹⁻²¹ leads to electron self-trapping²² on Ti, with associated displacement of neighboring ions. Thus

the electron behaves not as a Bloch function, but as a small polaron.²³⁻²⁶ The band structure computed with CRYSTAL06 yields a band gap of 3.76 eV, larger than experiment,²⁷ but otherwise the bands correspond well with those of earlier calculations and exhibit the complex nature of the lowest conduction bands.

Our calculations indeed predict that an extra electron within a TiO₂ supercell tends to localize, although 30% exchange potential is required for nearly complete localization on only one Ti.

When H_i is included in the CRYSTAL06 calculations, an interesting result emerges: depending on slightly different initial choices of atomic positions, slightly different minimum-energy atomic configurations emerge. And each of these exhibits spin localization on a different Ti! Thus the small-polaron nature of the electron persists, even when it comes from H_i. This result is in fact consistent with several published accounts²⁸⁻³⁰ in which either correlation or hybridization was included in the density functional formalism. We use these and other results to address the origin of the energy levels that emerge from analysis of the experimental results.

First we consider the three common sources of small splittings in vibrational spectra: (1) different heavy-atom isotopes, (2) H or D tunneling, (3) hindered rotation. Heavy-atom isotope shifts may be ruled out immediately because the isotopic abundances of ¹⁷O and ¹⁸O are too small to explain the observed spectra, and, also any splitting associated with “heavy” oxygen would be much larger than observed. Tunneling is also ruled out as the result of detailed calculations.³¹ CRYSTAL06 was used to calculate the potential energy function of H_i as a function of distance from O. The large relaxation characteristic of the O-H defect removes any potential tunneling degeneracy with respect to the O that lies across the channel, and even if that were not taken into account, the splitting would be orders of magnitude too small. In simple terms, the O-O distance across the channel is just too large for H or D to tunnel from one to the other. Rotational effects are also ruled out because the symmetry of rutile is so low that there is no axis of rotation for the OH complex lying in the xy plane. Attempts to simulate this using CRYSTAL06 yielded no productive results.

Instead, we believe that the energy splitting is associated with the near degeneracy of the small-polaron electron that arises from H_i and can localize on different Ti. This idea is consistent with EPR results^{7,8} that exhibit such localization on two distinctly different Ti atoms, depending on whether the electron comes from H_i or from substitutional F. The differences between the energies found by theory for configurations with the electron localized on different Ti are too small for theory to reliably determine their order.³² So the guidance of theory is general and not specific. Nonetheless, the combination of theory with experiment leads us to attribute the small splittings that are seen in IR experiments to small-polaron effects that are unique to TiO_2 .

In the context of the model shown in Fig. 4 to explain our experimental data, we propose that for E_1 the electron is localized on Ti_1 , consistent with EPR studies of neutral H at low temperature.⁸ For E_2 it is localized on Ti_2 . For E_3 it is localized on Ti_3 or Ti_3' , or on any one of many more distant Ti. This small polaron model provides a physical explanation for the three configurations with different energies that are required to explain the temperature dependence of our IR data.³² And the possibility that the electron can be localized on more distant Ti without affecting the OD frequency or energy of the configuration accounts for the high degeneracy found for E_3 (ref. 33).

IV. Conclusion

Our experimental results for OD in TiO_2 explain the difference between the IR spectra reported by Bates and Perkins⁶ in the 1970's and those of the recent study of Herklotz *et al.*⁹ We find results similar to BP for samples that are fully oxygenated to produce a charged OD^- center, whereas we find results similar to those reported by Herklotz *et al.* for samples reduced by annealing in D_2 to produce neutral OD.

While our temperature dependent IR data for the neutral OD center in TiO_2 are similar to the results reported by Herklotz *et al.*,⁹ we favor a different interpretation of these results. Herklotz *et al.* have suggested that the neutral OD center is a shallow donor in TiO_2 with a binding energy of 10 meV.³⁴ We, on the contrary, favor a small polaron model for the neutral charge state of OD in TiO_2 . Our spectra for samples reduced in D_2 show a neutral OD center whose total concentration remains constant throughout

the temperature range we have investigated (3.5K to 60K). The neutral OD center shows configurations with slightly different energies that arise from OD^- with an additional electron located on different Ti neighbors to produce the neutral center.³⁵ This model provides an explanation of IR results for the neutral OD center that is consistent with theory that finds that an electron becomes localized on Ti in TiO_2 and with the conclusions of recent EPR studies of H and F in TiO_2 .

V. Acknowledgements

We are grateful to R. Cappelletti for sending us the TiO_2 samples prepared by Bates and Perkins and also to G. Lüpke for the TiO_2 samples from Commercial Crystal Laboratories. We thank E. Lavrov, J. Weber, and G. D. Watkins for helpful discussions. K. Martin carefully read our manuscript and suggested several helpful improvements. The work at Lehigh University was supported by NSF Grant No. DMR 1160756. M.S. is grateful for support for visits to Dresden from the Humboldt Foundation.

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32. It should be noted that this assignment is not completely consistent with theoretical predictions²⁸⁻³⁰ (including ours), which indicate that the lowest-energy configuration places the electron on Ti₃ or Ti₃'. This is not consistent with EPR experiment (ref. 8), and the inaccurate theoretical ordering with

such small splittings may reflect issues such as defect-defect interaction associated with supercell size.

33. We recognize that using 3 levels to fit our data is a model and consider E_3 to be an effective energy for configurations with the extra electron located on more distant Ti atoms. In this same context, while the degeneracy $g_3=19$ was used to produce the fits to our data shown in Figs. 3 and 4, values of $g_3>12$ give satisfactory fits, suggesting that g_3 must be large and that the extra electron can be localized on a variety of more distant Ti sites. Note also the different roles played by the charged OD^- species in the present paper and in Ref. 9. Here, OD^- dominates in fully oxygenated samples, and an (OD^-) -like configuration also occurs for the neutral charge state as the polaron becomes localized on very distant Ti neighbors. In Ref. 9, OD^- is produced by the thermal ionization of the neutral, shallow OD center and gives rise to an IR line whose intensity grows at temperatures above near 20 K.
34. The shallow vs. deep character of H in TiO_2 remains puzzling. While several authors find evidence of a shallow, effective-mass-like, H center in TiO_2 , any possible relationship of a shallow H center to the O-H center studied in the present paper is not understood. See, for example, Ref. 9; S. F. J. Cox *et al.* J. Phys.: Condens. Matter **18**, 1079 (2006); and W. P. Chen, Y. Wang, and H. L. W. Chan, Appl. Phys. Lett. **92**, 112907 (2008).
35. OH centers are also present in our deuterated samples and give rise to a multi-line structure near 3290 cm^{-1} , similar to that reported in ref. 9. While we have been able to analyze the OH line shapes with a model similar to that used here for OD, the OH line shapes are broader and reveal less detail. We were not able to deduce useful information about isotope effects for the positions of the components of the three-line structure that is seen in IR spectra for OH vs OD.

Figure Captions

FIG. 1. IR absorption spectra ($T=4.2$ K, resolution 0.1 cm^{-1} , $[100]$ optical viewing direction) measured with $\mathbf{E} \perp \mathbf{c}$ for TiO_2 samples prepared by (a) Bates and Perkins (ref. 6) and (b) prepared at Lehigh. The samples in (a) were reported to have been deuterated by annealing in a D_2 ambient (5 h at 600°C) followed by an anneal in flowing oxygen (2 h at 800°C). The samples in (b) were deuterated by annealing in a D_2 ambient (4 h at 500°C). The lower spectrum was measured without further annealing. The upper spectrum was measured following a subsequent anneal in air (30 min at 500°C).

FIG. 2. (Color online) IR absorption spectra (resolution 0.1 cm^{-1} with $\mathbf{E} \perp \mathbf{c}$) measured as a function of temperature for a TiO_2 sample annealed in a D_2 ambient (4 h at 500°C). The upper traces show the IR spectra, as measured. The center traces show the spectra after the contribution from the line at 2445.0 due to the charged OD center has been subtracted. The lower traces show the fits to the center spectra by a sum of two Voigt line shapes.

FIG. 3. The areas of the absorbance curves, $A(\omega_H)$ and $A(\omega_L)$, measured as a function of temperature for the two components to the line shape assigned to the neutral OD center in TiO_2 . The solid lines show fits to the experimental data for the line areas. The dashed lines show the areas of the contributions arising from the levels E_1 and E_3 that sum to yield the area $A(\omega_L)$.

FIG. 4. (Color online) Semi-log plot of the ratio of the areas of the IR lines at ω_H and ω_L associated with the neutral OD center vs. inverse temperature. The solid line shows a fit to the data. The inset (upper right) shows the energies of the three configurations used to fit the temperature dependence of the IR data. The inset (lower left) show different configurations for the neutral OD center with a negative charge localized on different Ti^{3+} neighbors. [P. Ugliengo, D. Viterbo, and G. Chiari, *Z. Kristallogr.* **207**, 9 (1993); P. Ugliengo, "MOLDRAW: A program to display and manipulate molecular and crystal structures," Torino, 2006, available on the web at <http://www.moldraw.unito.it>.]

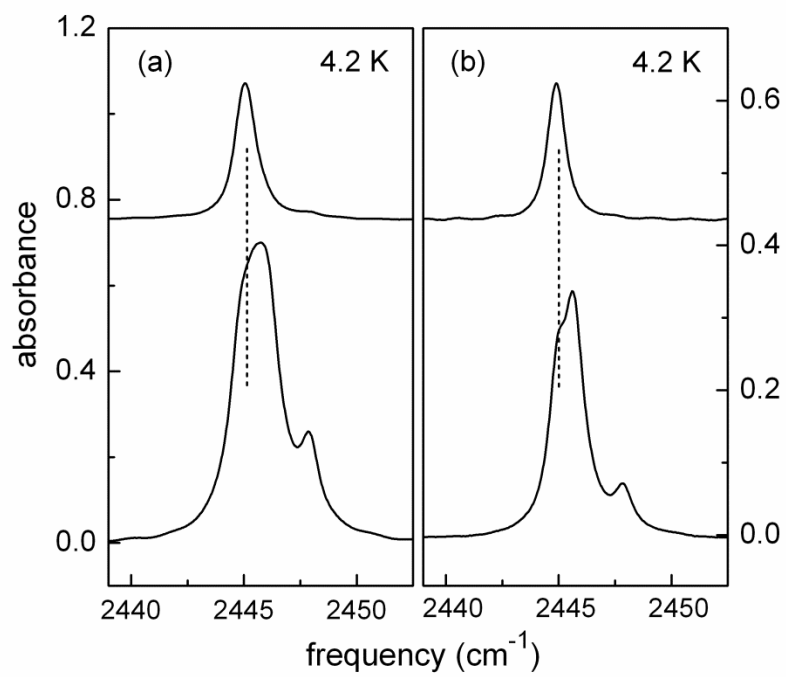


Fig. 1

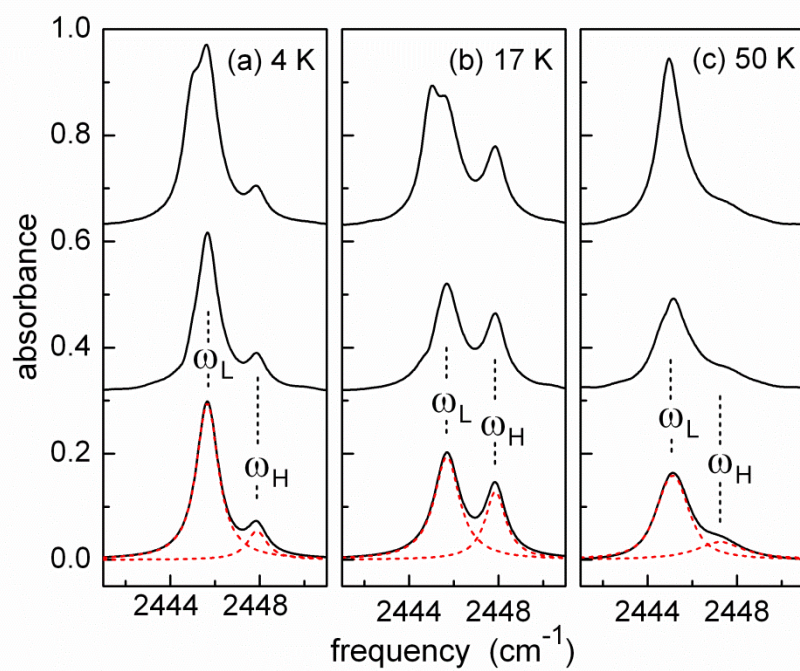


Fig. 2

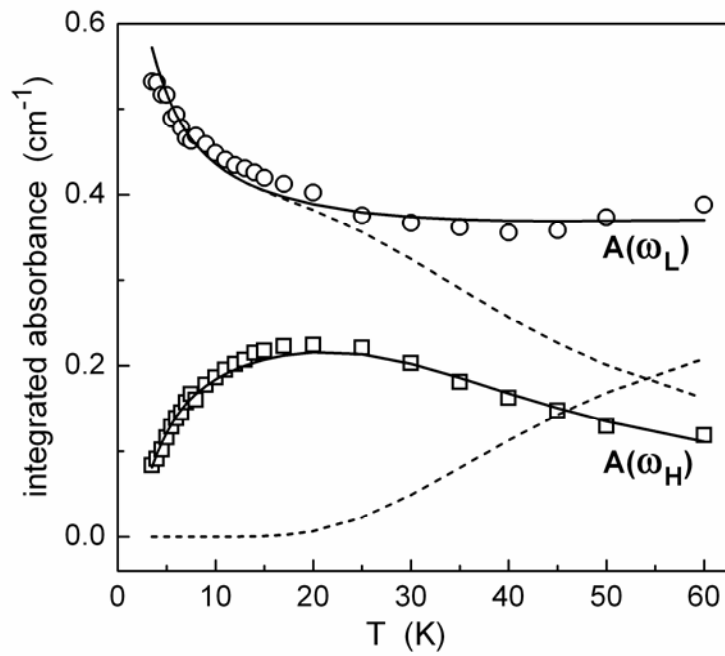


Fig. 3

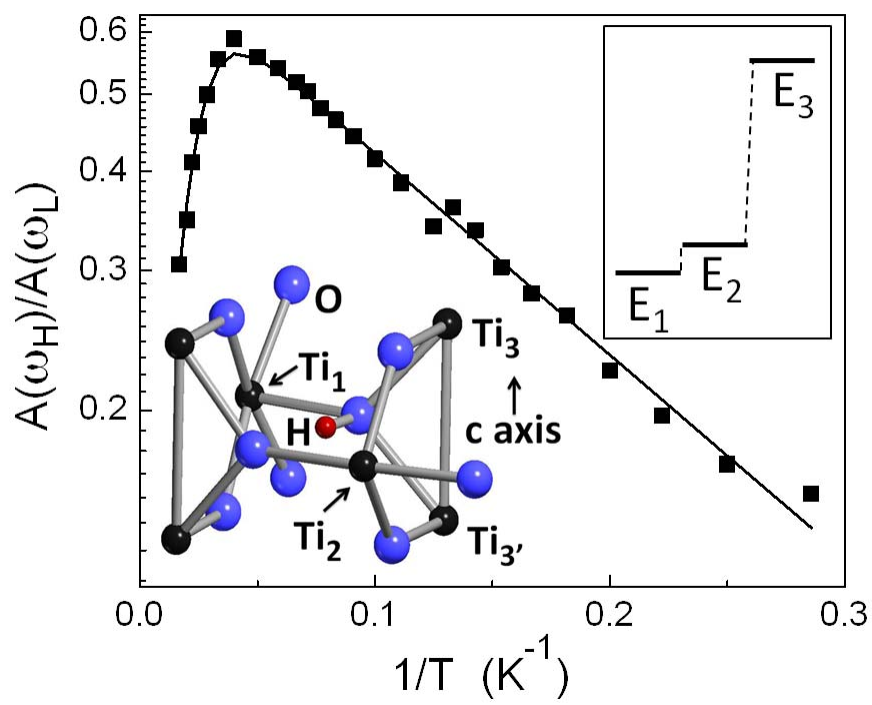


Fig. 4