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Lattice dynamics of RuO_2: Theory and experiment

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Although RuO_2 has been studied as a prototype catalyst for CO oxidation, no careful study of the lattice dynamics for this material has been presented so far. Using modern *ab initio* methods we obtain the phonon dispersion and the generalized density of states (GDOS). Inelastic neutron scattering experiments allow for an experimental determination of the GDOS. In contrast to what is known from structural studies, we find that the local density approximation gives a much better description of the phonon spectrum than the generalized gradient corrected form. This is also consistent with Raman measurements. Our findings have important consequences for all quantities depending on the phononic part of the free energy.

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Recently transition metal oxides have received a lot of attention mostly based on their importance for applications in electrochemistry,[1] catalysis,[2] and ferroelectric random access memories.[3] Especially, RuO_2 has been studied in great detail to understand the mechanism for the catalytic carbon monoxide oxidation on $RuO_2(110)$ surface.[2] Density functional calculations have been applied to this system with great success;[4–6] however, a detailed understanding of the above-mentioned phenomena requires a proper treatment of temperature and pressure. The concept for dealing with these complications is known under the name of "*ab initio* thermodynamics." However, while treating temperature and pressure effects of the gas phase explicitly, the solid-state components of the system have been dealt with only in an approximate way. Temperature effects are usually treated in an Einstein model and are estimated in most cases to be negligible.[4] Modern *ab initio* density functional perturbation theory offers these days a parameter-free calculation of lattice dynamics. It thus allows the determination of the phononic contribution to the free energy without the necessity for simplifying assumptions. Despite its importance no *ab initio* study of the lattice dynamics of RuO_2 has been reported so far. In this paper we present such studies of the lattice dynamics of bulk RuO_2 in the rutile structure and compare our results with Raman measurements[7] as well as with measurements of the generalized phonon density of states obtained by inelastic neutron scattering. In a forthcoming publication we will present results for the lattice dynamics of $RuO_2(110)$ surface. Together with the bulk studies presented here we will be able to determine the vibrational part of the surface free energy from *ab initio* theory.

Calculations of the structure and the lattice dynamics are performed in the framework of density functional theory with the mixed-basis pseudopotential method. The linear response technique has been used for obtaining the vibrational modes.[8] Pseudopotentials were constructed following the description of Vanderbilt[9] where for Ru the 4*s* and 4*p* semicore states were treated as valence electrons as well as the oxygen 2*s* states. Inclusion of the Ru semicore states improved the agreement with all electron calculations with the WIEN2k code[10] substantially.

The mixed-basis scheme uses a combination of local functions and plane waves for the representation of the valence states.[11,12] This allows for an efficient treatment of the fairly deep *s*, *p*, and *d* potentials of Ru and the *s* and *p* potentials of O. Supplementary plane waves were taken into account up to a kinetic energy of 22 Ry. For the exchange-correlation functional the local density approximation (LDA) as given by Hedin and Lundqvist[13] and the generalized gradient approximation (GGA) as given by Perdew, Becke, and Ernzerhof[14] (PBE) have been applied. Brillouin-zone (BZ) integrations were performed using a tetragonal *k*-point mesh of Monkhorst-Pack type[15] in connection with the standard smearing technique employing a Gaussian broadening of 0.2 eV. Sufficient convergence of the ground state and the phonon calculations were achieved with a $8\times8\times16$ mesh corresponding to 80 *k* points in the irreducible wedge of the BZ (IBZ). Dynamical matrices were calculated on a $4\times4\times4$ grid (18 points in the IBZ) from which phonon dispersions were obtained by standard Fourier interpolation.[16,17]

Having discussed so far the theoretical treatment we now present the results. The rutile structure is characterized by the external cell parameters V and c/a and an internal parameter u. Optimized values are listed in Table I where LDA and GGA results are given as obtained from pseudopotential calculations as well as from all-electron studies with the WIEN2k code.[10] The all-electron calculations were carried out with the following parameters: $R_{MT}^{Ru}=2.0$ bohrs, R_{MT}^{O}

TABLE I. Structural parameters of RuO_2 rutile. Comparison of various LDA and GGA calculations with experimental results taken from Ref. 18.

		V (Å^3)	c/a	u	B (GPa)
LDA	All-*e*	60.76	0.6972	0.3072	315
	Pseudo	60.08	0.6944	0.3065	314
GGA	All-*e*	64.19	0.6930	0.3067	268
	Pseudo	63.06	0.6893	0.3058	255
Expt.		62.6	0.6918	0.3057	270

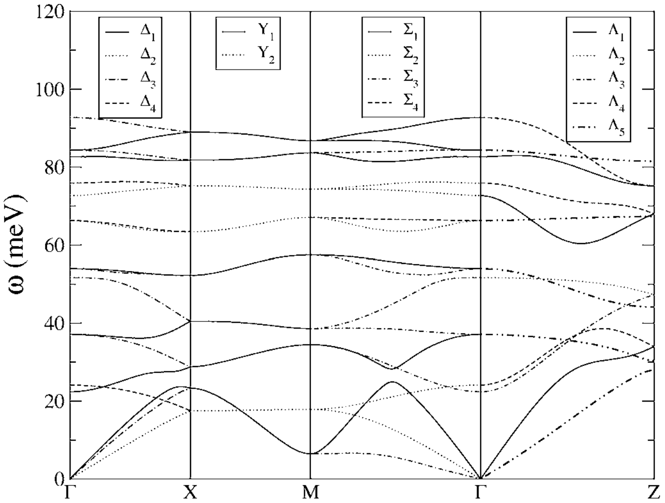

FIG. 1. Calculated phonon dispersion for RuO_2 (rutile) with the LDA along high-symmetry lines.

=1.5 bohrs, $E_{max}^{wf}=36$ Ry, $E_{max}^{pot}=324$ Ry, and the wave function and potential expansion inside the muffin tins up to $l_{max}^{wf}=10$ and $l_{max}^{pot}=4$, respectively. For k-point sampling a $8\times 8\times 12$ Monkhorst-Pack grid has been used with a Gaussian smearing of 0.2 eV. As can be seen the pseudopotential results are in very good agreement with the all-electron calculations. Comparing with the experimental results we see that the LDA underestimates the volume by roughly 3% while the GGA overestimates the volume by slightly over 2%. The ratio c/a and the internal parameter u agree with the experimental findings to better than 1% for the LDA as well as for the GGA treatment. Our structural results are similar to those given in Refs. 19 and 20.

Using these optimized structures the phonon dispersion and the generalized phonon density of states (GDOS) have been calculated as indicated above. Phonon dispersions are presented in Fig. 1 (LDA) and Fig. 2 (GGA). We have included the symmetry labeling of the phonon modes. Details can be found in Refs. 21 and 22 where the symmetry classes of the rutile structure have been discussed extensively. Analysis of the eigenvectors shows that Ru-dominated modes are responsible for the low-lying part of the spectrum, while above 50 meV the spectrum is clearly oxygen dominated.

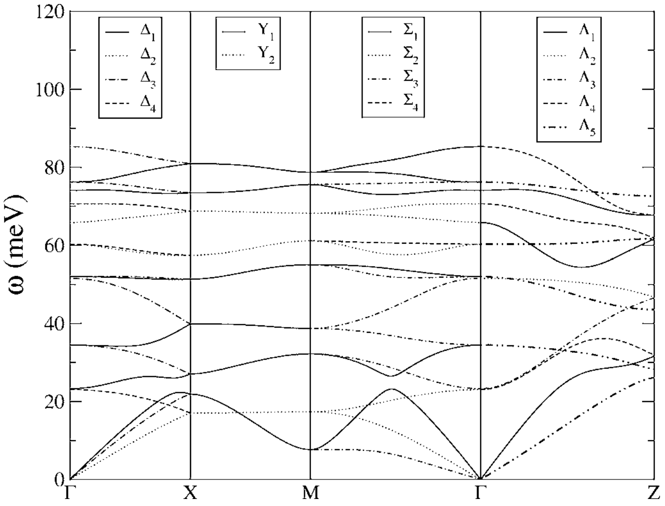

FIG. 2. Calculated phonon dispersion for RuO_2 (rutile) with the GGA along high-symmetry lines.

TABLE II. Elastic moduli C_{ij} and bulk modulus B (Voigt notation, 10^{12} dyn/cm^2) as obtained from the calculated phonon spectra with the LDA and GGA.

	C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}	B
LDA	3.36	6.57	1.19	2.68	3.00	2.37	3.04
GGA	2.99	5.58	1.14	2.27	2.46	1.99	2.58

Comparing LDA and GGA dispersions the most striking difference is seen at the upper end of the spectrum. For the GGA the high-lying oxygen modes are located around 70 meV while in LDA calculations they show up around 80 meV which is a very significant difference. Selected frozen phonon calculations with the all-electron code confirm this difference between LDA and GGA results, eliminating the possibility that it is an artifact of the pseudopotential treatment. The low-lying modes, however, are in general very similar in the GGA and LDA, reflecting only the different elastic constants for $q\rightarrow 0$. In Table II we have summarized all elastic constants as obtained from the $q\rightarrow 0$ limit of the phonon calculations. As can be seen, results for the bulk modulus obtained in this way are very similar to the bulk modulus values obtained directly from structural optimization calculations as given in Table I. This demonstrates the high internal consistency of structural and phonon calculations. For comparison with experimental data so far only $q=0$ modes obtained from Raman measurements[7] are available. These modes are listed in Table III and compared with our calculations. As can be seen the most prominent E_g mode is represented very well in LDA calculations, while in GGA calculations the frequency of this mode is substantially underestimated. For other modes the effect is not as drastic but, also, here the experimental results favor the LDA compared to the GGA. However, these measurements probe only the Γ point of the BZ; thus, statements about the quality of the LDA versus the GGA might be misleading. To overcome this problem we have measured the GDOS with neutron scattering and compared with our calculated GDOS. Before discussing experimental and theoretical results we will concentrate now on the experiment.

For inelastic neutron spectroscopy (INS) measurements at

TABLE III. Comparison of measured and calculated frequencies of Raman-active modes (in meV).

	Experiment	Theory	
	(Ref. 7)	LDA	GGA
B_{1g}	20.5	22.4	23.2
E_g	65.2	66.3	60.3
A_{1g}	80.0	82.7	74.1
B_{2g}	88.7	92.7	85.3

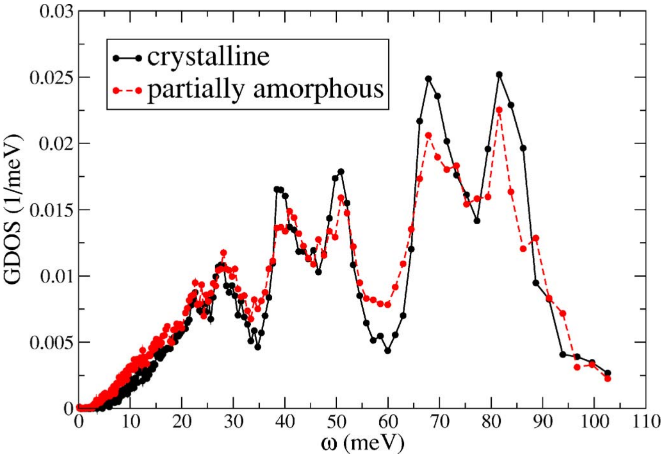

FIG. 3. (Color online) Experimental generalized density of states (GDOS) for crystalline and partially amorphous RuO_2 as obtained by inelastic neutron scattering.

300 K the IN6 time-of-flight spectrometer at the high-flux reactor in Grenoble (France) was used in the upscattering mode with an incident neutron energy of 4.8 meV. A high chopper speed (14868 rpm) and focusing in the inelastic region were chosen to optimize the resolution which, due to the energy-gain mode, becomes worse for large energy transfers, where we estimate $\Delta\hbar\omega$ (FWHM) $\approx$5 meV. The INS experiments sample the entire Brillouin zone and thus allow one to extract the GDOS which, in our case, is corrected for multiphonon contributions via a self-consistent procedure. The GDOS is a sum of the partial densities of states of Ru and O weighted by σ/m (neutron scattering cross section over the mass).

For our samples we used commercial RuO_2 powder which turned out to be amorphous. Crystalline RuO_2 was obtained by annealing at 900 °C. Results are shown in Fig. 3 where additionally we show the spectrum of a sample which was annealed at 500 °C with still amorphous contributions. For all investigated samples drying at 300 °C and sealing into airtight cylinders was necessary to avoid the adsorption of water. All materials were checked by x-ray analysis where the $P4_2/mnm$ (No. 136) structure for crystalline RuO_2 was confirmed. The amorphous contributions lead to an increased GDOS at low energies and a reduction of weight at the upper region of the spectrum; however, peak positions are only slightly influenced.

Now we will concentrate on a comparison between experiment and theory. Figure 4 shows the calculated GDOS results for the LDA and GGA together with the experimental results for the crystalline samples. The calculated spectra have been broadened with a Gaussian distribution with a width of 4 meV to simulate the experimental resolution at higher energies. In the regime up to 20 meV which is dominated by Ru vibrations LDA and GGA results do not differ appreciably and both agree very well with the experiment. Above roughly 20 meV the LDA and GGA start to differ more and more with the phonon modes calculated by the GGA being much softer. Above 60 meV it becomes quite obvious that the GGA results do not agree with the experiments while the LDA gives very good agreement with the measured generalized phonon density of states. In the upper part of the spectrum the GGA results are off by roughly 10 meV which is a huge discrepancy especially in view of the high accuracy achievable in *ab initio* phonon calculations these days. The measurements of the GDOS support trends already seen in Raman measurements and indicate that these are not restricted to the Γ point in the BZ only. While for structural studies it seems that GGA calculations give a slightly better description compared to experiment than the LDA, for investigations of phonon properties the LDA is clearly to be preferred.

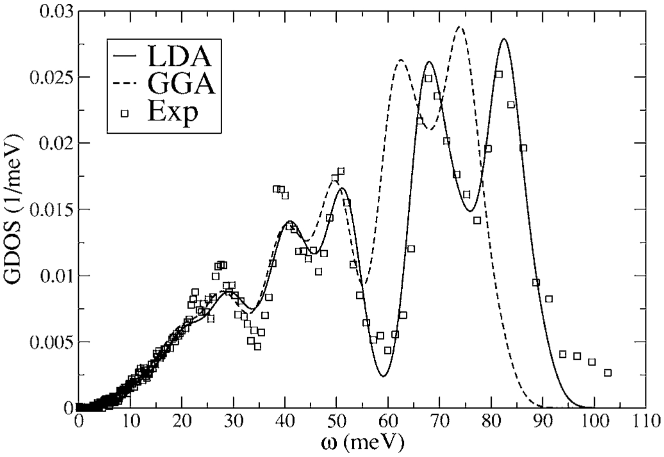

FIG. 4. Comparison of theoretical GDOS results for the LDA and GGA with experimental data for the crystalline sample.

To get a better understanding of the origin of these large differences between the phonon spectra for the LDA and GGA we have tried to separate purely structural effects from those related to the different correlation treatment. Using GGA structural parameters in an LDA phonon calculation led to even slightly softer oxygen modes than in the pure GGA treatment. Thus it is clear that the softening in the GGA compared to the LDA is mostly a structural effect with only small modifications due to the different correlation treatment.

Our results have of course important consequences for thermodynamic quantities. Knowledge of the phonon density of states allows for a calculation of the vibrational contribution of the free energy.[4] For RuO_2 we find that at $T=300$ K the results for the free energy in the LDA and GGA differ by 40 meV. This difference grows with increasing temperature since the upper part of the phonon spectrum gets more and more populated and LDA studies favor a much harder spectrum than the GGA.

In summary, we have shown that modern *ab initio* treatments of the bulk lattice dynamics of important catalysts are possible; however, contrary to the generally accepted view that GGA studies are most appropriate for RuO_2, we could show that LDA results for the lattice dynamics are superior to those obtained with the GGA with important consequences for all studies which involve temperature. This is concluded by the comparison with Raman measurements and with new results obtained from inelastic neutron scattering as well. The consequences of these findings for surfaces will be discussed in a forthcoming publication.[23]

[1] D. R. Rolison, P. L. Hagans, K. E. Swider, and J. L. Long, Langmuir **15**, 774 (1999).

[2] H. Over, Y. D. Kim, A. P. Seitsonen, S. Wendt, E. Lundgren, M. Schmid, P. Varga, A. Morgante, and G. Ertl, Science **287**, 1474 (2000).

[3] Suk-Kyoung Hong, Hyeong Joon Kim, and Hong-Geun Yang, J. Appl. Phys. **80**, 822 (1996).

[4] K. Reuter and M. Scheffler, Phys. Rev. B **65**, 035406 (2001).

[5] K. Reuter and M. Scheffler, Phys. Rev. B **68**, 045407 (2003).

[6] Q. Sun, K. Reuter, and M. Scheffler, Phys. Rev. B **70**, 235402 (2004).

[7] S. S. Rosenblum, W. H. Weber, and B. L. Chamberland, Phys. Rev. B **56**, 529 (1997).

[8] R. Heid and K.-P. Bohnen, Phys. Rev. B **60**, R3709 (1999).

[9] D. Vanderbilt, Phys. Rev. B **32**, 8412 (1985).

[10] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, computer code WIEN2k, an augmented plane wave+local orbitals program for calculating crystal properties, Karlheinz Schwarz Technical University, Wien, Austria, 2002.

[11] S. G. Louie, K.-M. Ho, and M. L. Cohen, Phys. Rev. B **19**, 1774 (1979).

[12] B. Meyer, C. Elsässer, and M. Fähnle, FORTRAN90, a program for mixed-basis pseudopotential calculations for crystals, Max-Planck-Institut für Metallforschung, Stuttgart.

[13] L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971).

[14] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[15] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[16] P. Giannozzi, S. de Gironcoli, P. Pavone, and S. Baroni, Phys. Rev. B **43**, 7231 (1991).

[17] X. Gonze and C. Lee, Phys. Rev. B **55**, 10355 (1997).

[18] R. M. Hazen and L. W. Finger, J. Phys. Chem. Solids **42**, 143 (1981).

[19] K. M. Glassford and J. R. Chelikowsky, Phys. Rev. B **47**, 1732 (1993).

[20] J. S. Tse, D. D. Klug, K. Uehara, Z. Q. Li, J. Haines, and J. M. Léger, Phys. Rev. B **61**, 10029 (2000).

[21] J. G. Traylor, H. G. Smith, R. M. Nicklow, and M. K. Wilkinson, Phys. Rev. B **3**, 3457 (1971).

[22] J. G. Gay, W. A. Albers, Jr., and F. J. Arlinghaus, J. Phys. Chem. Solids **29**, 1449 (1968).

[23] K.-P. Bohnen, R. Heid, and O. de la Peña Seaman (unpublished).