Optical properties of PdO and PtO

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(Received 24 January 1994)

We have calculated the anisotropic dielectric function for PdO and PtO using the linear-muffin-tin-orbital method in atomic-sphere-approximation. The optical matrix elements are explicitly included in the calculations and we find that they play a significant role in determining the shape of the frequency dependence of the dielectric function and its anisotropy. Our calculated dielectric functions for PdO are compared with the recent data of Weber *et al.* The agreement is good although the calculations show more features than are observed experimentally and give a band gap that is too small by about 0.6 eV. For PtO there are no experimental data available. We conclude that for these two transition-metal monoxides an itinerant description of the d states is appropriate.

I. INTRODUCTION

The nonmagnetic transition-metal monoxides PdO and PtO have been found to have important technological applications related to automotive catalysts. So far their basic electronic properties have only been studied in a few articles. On the other hand, the related $3d$ transition-metal monoxides have been extensively studied[1–8] due to their highly correlated ground-state properties, giving rise to insulating and magnetic behavior. Nevertheless, the electronic structure of NiO, for example, is still a controversial subject. Since Pd and Pt are situated right below Ni in the Periodic Table, it becomes of particular interest to understand the electronic properties of PdO and PtO, so that they can be compared with or contrasted to the properties of NiO. In the case of NiO it is believed that the band gap originates from strong correlation effects among the localized $3d$ electrons of Ni. NiO is an antiferromagnet with a cubic sodium chloride structure, while PdO and PtO , i.e., compounds with $4d$ and $5d$ electrons, have a tetragonal crystal symmetry.[9,10] They are nonmagnetic but are insulators, sharing the latter property with NiO. A relevant question then becomes whether or not this insulating behavior derives from strong electron-electron correlation such as in NiO. Since the $4d$ and $5d$ orbitals are more diffuse than the $3d$ orbitals in NiO, one could expect, however, that the electron interactions will be comparatively weak. If this is the case, this in turn suggests that band theory should be valid for these two oxides. Brandow[1] and Goodenough[2] have argued that the lower symmetry tetragonal structure is favored in these compounds because even in a conventional band picture it allows for the creation of crystal-field band gaps which lower the total energy of the system. Recently, Hass and Carlsson[11] have reported a density functional band calculation within the local-density approximation (LDA) for PdO and PtO using the augmented spherical wave (ASW) method. Their calculations seem to support the above-mentioned picture of the electronic structure, namely that PdO and PtO are relatively well behaved electronically. For example, it was calculated that PdO and PtO have direct energy band gaps of 0.1 eV and 0.7 eV, respectively, at the symmetry point M. These calculated gaps are smaller than the gaps deduced from the optical measurements. However, such band gap discrepancies are common in LDA theory. Major features in the density of states were identified by Hass and Carlsson[11] but no attempt was made to relate them to optical data. Recently, Weber *et al.*[12] have measured the dielectric functions $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ for the optical electric vector oriented parallel and perpendicular to the c axis, respectively, for an energy range 1.6–5.8 eV by ellipsometric techniques. In these experiments they observed a strong anisotropy. It would, therefore, be worthwhile to calculate these two dielectric functions and compare them with data. In this way we could obtain important additional evidence regarding the nature of the

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electronic structure in the $4d$ and $5d$ monoxides. Also, it is of interest to investigate to what extent parameter-free calculations can account for anisotropic optical properties, something which has not yet been studied very much by modern electronic structure calculations.

With this in mind we present calculations of the imaginary part of the dielectric function for the electric vector parallel and perpendicular to the c axis. Our calculations are performed using the linear-muffin-tin-orbital method[13,14] in the atomic-sphere approximation (LMTO-ASA). The optical matrix elements are explicitly calculated as they are expected to play a significant role in the frequency dependence of the dielectric functions and their anisotropy. We also compare our band structures with those of Hass and Carlsson and find good agreement.

II. DETAILS OF CALCULATIONS

The calculations are done at the measured lattice constants of a=3.043 Å and c=5.3363 Å for PdO (Ref. 9) and a=3.077 Å and c=5.3400 Å for PtO.[10] PdO and PtO are loosely packed crystals and hence they are not directly suitable for conventional LMTO-ASA calculations. A common way to remedy such an unfavorable physical situation is to introduce empty spheres at appropriately chosen interstitial sites.[15,16] We have chosen to introduce four such empty spheres. The calculations are performed with equal sphere radii and a basis consisting of s, p, and d LMTO's at each site. Scalar relativistic corrections are included but spin-orbit coupling is neglected for convenience. For PtO one would expect a significant effect on the d density of states from the spin-orbit interaction, while for PdO this will only give a minor change. Since at present there are no experimental optical data available for PtO, we have chosen to treat PtO in the same way as PdO, i.e., without spin-orbit coupling. The Barth-Hedin[17] local exchange-correlation functional is used. To obtain a converged potential and/or charge density a grid of 196 $\vec{k}$ points is taken in the irreducible Brillioun zone (IBZ).

For a tetragonal structure we need to calculate two components of the total imaginary dielectric function $\mathrm{Im}\epsilon_{\mathrm{tot}}(\omega)$, corresponding to light polarized parallel and perpendicular to the c axis. These components[18,19] are (in atomic units)

$$\mathrm{Im}\epsilon_{\parallel}(\omega) = \frac{12}{m\omega^2}\int_{\mathrm{BZ}}\sum_{nn'}\frac{|P^z_{nn'}(\vec{k})|^2 dS_k}{\nabla\omega_{n'n}(\vec{k})} \tag{1}$$

and

$$\mathrm{Im}\epsilon_{\perp}(\omega) = \frac{6}{m\omega^2}\int_{\mathrm{BZ}}\sum_{nn'}\frac{[|P^x_{nn'}(\vec{k})|^2 + |P^y_{nn'}(\vec{k})|^2]dS_k}{\nabla\omega_{n'n}(\vec{k})}, \tag{2}$$

where ω is the photon energy (Ry) and $\mathrm{P}^x_{nn'}(\vec{k})$ is the x component of the dipolar matrix element between the initial $|n\vec{k}\rangle$ and final $|n'\vec{k}\rangle$ states. $\mathrm{E}_n(\vec{k})$ and $\mathrm{E}_{n'}(\vec{k})$ are their respective eigenvalues, and $\omega_{n'n}(\vec{k})$ is the energy difference

$$\omega_{n'n}(\vec{k}) = E_{n'}(\vec{k}) - E_n(\vec{k}) \tag{3}$$

and S_k is the constant energy (ω) surface. The total imaginary part of $\epsilon_{\mathrm{tot}}(\omega)$ is given by

$$\mathrm{Im}\epsilon_{\mathrm{tot}}(\omega) = \frac{\mathrm{Im}\epsilon_{\parallel}(\omega) + 2\mathrm{Im}\epsilon_{\perp}(\omega)}{3}. \tag{4}$$

III. RESULTS AND DISCUSSIONS

First of all we notice that our presently calculated energy band structures are in good agreement with those of Hass and Carlsson.[11] Thus we find that both PdO and PtO are semiconductors with a minimum direct gap of 0.1 eV for PdO and 0.6 eV for PtO, respectively, occurring at the symmetry point $M(\pi/\mathrm{a},\pi/\mathrm{a},0)$. These gaps are in rather good agreement with the results of the ASW calculations of Hass and Carlsson.[11] For PdO the measured gap is 0.7 eV while for PtO it is even larger.[11] Therefore, there is a disagreement between theory and experiment, since the theoretical band gap underestimates the gap in PdO by 0.6 eV. On the other hand, it is well known that LDA theory in general underestimates band gaps for semiconductors. Thus to get the correct value of the gap one probably would need to include correlations similar to those used for Si.[20]

The density of states (DOS) for PdO and PtO are shown in Figs. 1 and 2. Our DOS are similar to the ones obtained by Hass and Carlsson.[11] We also show the d-partial DOS for the transition-metal and p-partial DOS for oxygen in the same figures. The main structures in the DOS are dominated by the transition-metal d-states near the Fermi level with a significant contribution from the oxygen p states away from the Fermi level. Our calculations for PdO yield main structures at −0.50, −0.35,

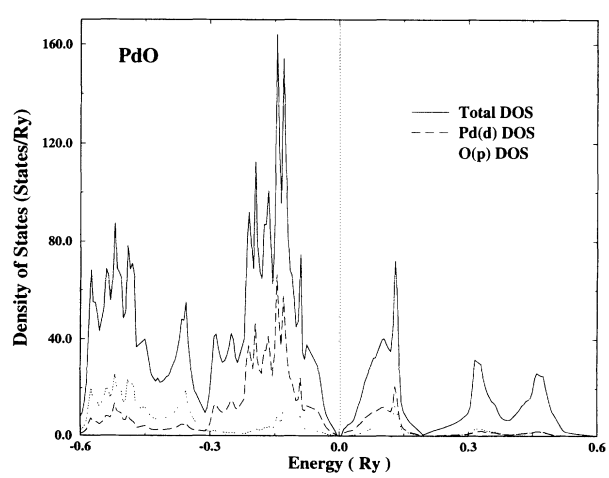

FIG. 1. Calculated density of states for PdO. The full line shows the total DOS, while the dashed and dotted lines show the d-partial and p-partial DOS per atom for Pd and O, respectively. The Fermi level is set at zero energy and marked by a vertical line.

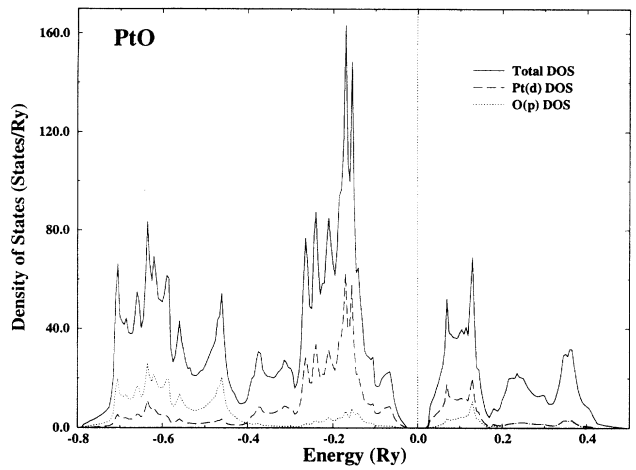

FIG. 2. Calculated density of states for PtO. The full line shows the total DOS, while the dotted and dashed lines show the d-partial and p-partial DOS per atom for Pt and O, respectively. The Fermi level is set at zero energy and marked by a vertical line.

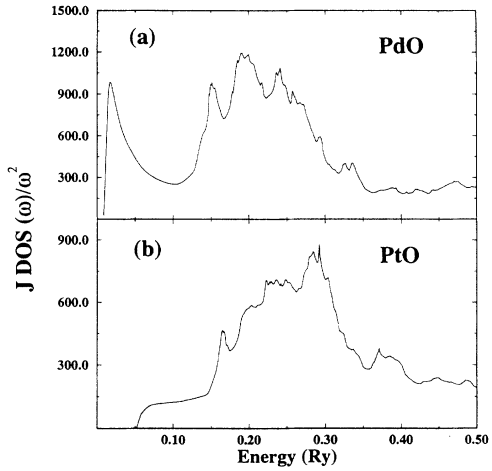

FIG. 3. The calculated energy weighted joint density of states JDOS(ω)/ω^2 (a) for PdO and (b) for PtO.

and -0.15 Ry and these are in agreement with the ASW calculations as well as with the photoemission data.[21] For PtO the main structures are at -0.65, -0.45, -0.25, and -0.15 Ry. We conclude that PdO and PtO are strikingly similar and that the main difference is the considerably larger band gap for PtO than for PdO. The $X\alpha$ cluster calculations[22] support this difference as do preliminary optical measurements.[23]

The recent measurement of the anisotropic optical dielectric response of PdO by Weber *et al.*[12] is the prime motivation of this work. Weber *et al.*[12] have measured the dielectric response functions of single crystal PdO parallel and perpendicular to the c axis for the energy range 1.6–5.8 eV. In the absence of any theoretical calculation, they chose to explain the $\epsilon_{\parallel}(\omega)$ and $\epsilon_{\perp}(\omega)$ by a Lorentz-oscillator-type response near 2.5 eV, but where the oscillator strength for $\epsilon_{\parallel}$ is about twice that for $\epsilon_{\perp}$. Previous optical measurements[24,25] were performed on unoriented polycrystalline PdO made by completely oxidized films of Pd sputtered or evaporated onto quartz substrates.

Before we show the results from our full calculation of the dielectric function, we choose to present our calculated joint density of states (JDOS). This quantity, JDOS(ω), is of interest since the dependence on the optical transition matrix elements is then totally neglected. The results for PdO and PtO are shown in Fig. 3. What we have plotted is actually JDOS(ω)/ω^2 because this is equal to $\epsilon(\omega)$ for the case when the optical matrix elements are equal to unity. We have used 196 $\vec{k}$ points to calculate JDOS. Previous experience indicates that even a smaller number of $\vec{k}$ points is sufficient to give converged values of JDOS and $\epsilon(\omega)$.[26] For both oxides JDOS(ω)/ω^2 starts at the minimum gap (0.1 eV for PdO and 0.6 eV for PtO) demonstrating that the grid of 196 $\vec{k}$ points is sufficient to bring out the onset of optical transitions. As can be seen there is a lot of structure in the JDOS(ω)/ω^2 curves, the primary peaks being around 0.03 Ry and 0.2 Ry for PdO and around 0.25 Ry for the PtO. It would seem tempting to identify the 0.2 Ry structures in PdO with the experimentally observed structure at 2.5 eV. Such an assignment is only tentative and one should really include the optical matrix elements in the calculations before a detailed comparison between theory and experiment is attempted. This will be done below.

Next the calculations are performed for Im$\epsilon_{\parallel}(\omega)$, Im$\epsilon_{\perp}(\omega)$, and Im$\epsilon_{\rm tot}(\omega)$ including the effect of the optical matrix elements. The results for PdO are plotted in Fig. 4 together with experimental data. First of all we notice that the theoretical curves show more structure than the experimental data. This is due to the fact that the experimental data has an inherent broadening

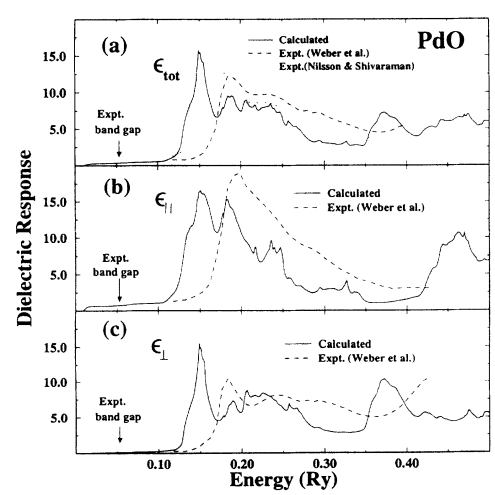

FIG. 4. (a) Comparison between the calculated and experimental Im$\epsilon_{\rm tot}$ for PdO. The dashed line shows the single crystal data from Weber *et al.* (Ref. 12) and the dotted line shows the polycrystalline data from Nilsson and Shivaraman (Ref. 25). (b)Comparison between the calculated and experimental (Ref. 12) Im$\epsilon_{\parallel}$ for PdO. (c) Comparison between the calculated and experimental (Ref. 12) Im$\epsilon_{\perp}$ for PdO.

that is not included in the calculations. Consider first $\mathrm{Im}\epsilon_{\mathrm{tot}}$ which has been plotted in Fig. 4(a). Major calculated features occur at 0.15, 0.20, 0.38, and 0.47 Ry. There seems to be good agreement between the shape of the calculated $\mathrm{Im}\epsilon_{\mathrm{tot}}(\omega)$ and the shape of the measured $\mathrm{Im}\epsilon_{\mathrm{tot}}(\omega)$. Both curves show a sharp increase at about 0.15 Ry above the first onset of the optical transitions. After going through a peak, the experimental $\mathrm{Im}\epsilon_{\mathrm{tot}}(\omega)$ decreases with increasing energy. The theoretical curve shows a similar trend although with more structures. Experiments show a rather flat region around 0.23 Ry which can be identified with the structure around 0.18–0.23 Ry. Thereafter, both the experimental and theoretical curves show a decrease in $\mathrm{Im}\epsilon_{\mathrm{tot}}(\omega)$. Displacing the theoretical energy curve by 0.05 Ry towards higher energy, a good agreement can be obtained between theory and experiment. As already mentioned, this shift corresponds exactly to what is needed to bring the experimental and theoretical band gaps into agreement.

The calculated parallel dielectric function for PdO is compared with experiments in Fig. 4(b). The sharp rise in $\mathrm{Im}\epsilon_{\parallel}(\omega)$ is present in both curves except that in experiment it occurs at a higher energy (by about 0.05 Ry above the theory curve). After peaking at 0.2 Ry the experimental $\mathrm{Im}\epsilon_{\parallel}(\omega)$ drops with increasing energy. The calculated $\mathrm{Im}\epsilon_{\parallel}(\omega)$ also drops but only after going through some secondary peaks around 0.19, 0.24, and 0.33 Ry. The first two of these peaks might be associated with the shoulders at 0.24 and 0.29 Ry seen in the experimental curve. The third theoretical peak at 0.33 Ry is probably not pronounced enough to give rise to any clear feature in the experimental data. Again we notice that by displacing the theoretical curve by 0.05 Ry towards higher energy, a very good agreement with the experimental data is obtained, since the theoretical peak positions then agree with the positions of the experimental shoulders.

The calculated $\mathrm{Im}\epsilon_{\perp}(\omega)$ is compared with experiment in Fig. 4(c). The experimental $\mathrm{Im}\epsilon_{\perp}(\omega)$ shows peaks at 0.20 and 0.25 Ry, thereafter there is a decrease and then an increase around 0.40 Ry. As in the case for the total and the perpendicular dielectric functions, there is a shift of 0.05 Ry between the experimental and the calculated onset of optical transitions. If the two onsets are matched, good agreement between theory and experiment is obtained over the whole range of energy where there are experimental data available.

Thus, with the exception of the absolute value for the energy band gap, we have found good agreement between experiment and theory for PdO. We like to stress that the observed pronounced anisotropy is well reproduced by the present calculations. We conclude that a band theoretical approach is appropriate for the description of the electronic structure of PdO.

In Fig. 5, we show the calculated dielectric response for PtO. No experimental data have so far been reported for this material, but we hope our work will motivate further experimental work on PtO. At the onset of the first strong feature it is clear that anisotropy effects are equally pronounced in PtO as in PdO. For example, the structures at 0.16 and 0.28 Ry in the total dielectric response are clearly dominated by contributions from $\epsilon_{\perp}$ while those around 0.20 and 0.37 Ry originate from $\epsilon_{\parallel}$. The structure at 0.48 Ry has contributions both from $\epsilon_{\parallel}$ and $\epsilon_{\perp}$.

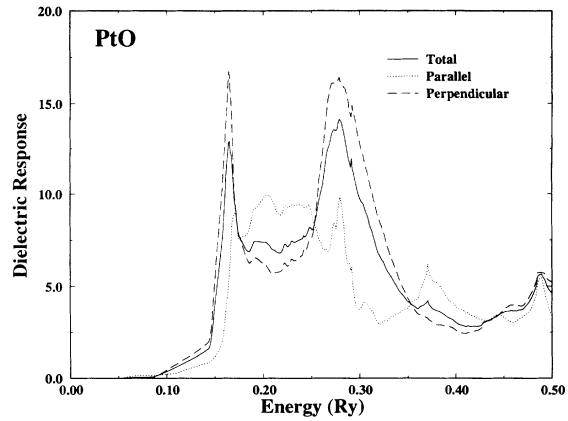

FIG. 5. Different (perpendicular and parallel) components of the calculated $\mathrm{Im}\epsilon$ for PtO.

The total dielectric response of PtO shows major peaks at 0.15 and 0.28 Ry with pronounced dips around 0.2 and 0.4 Ry, whereas for PdO pronounced peaks occur at 0.15 and 0.38 Ry with a flattening around 0.2 Ry and a dip around 0.3 Ry. Thus the total dielectric response for PdO and PtO show similarities except that the positions of the structures are different. The anisotropy of dielectric response is however of different nature in the two materials.

IV. CONCLUSIONS

We have calculated the anisotropic dielectric response for PdO and PtO using the LMTO-ASA method. Our present density of states shows all the features found in a recent calculation by Hass and Carlsson using the ASW method.[11] We find smaller energy gaps for PdO and PtO than observed experimentally, indicating the need for going beyond the LDA and to include further correlations. The calculated $\epsilon(\omega)$ for PdO shows more structure than is observed experimentally. If our primary interest had been to fit the data, this could have been done by introducing a phenomenological relaxation time τ giving rise to a broadening. All the calculated $\epsilon(\omega)$ functions show a sharp rise at low energies indicating the onset of strong optical transitions and this is in agreement with experiment on PdO except that there is an energy misfit by about 0.05 Ry. Apart from this there is good agreement with the data. We hope that our calculations will stimulate measurements of the anisotropic dielectric response in PtO. Based on the present successful account of the observed anisotropy of the optical properties for PdO, as well as the detailed features of the experimentally measured $\mathrm{Im}\epsilon_{\parallel}$ and $\mathrm{Im}\epsilon_{\perp}$ functions, we conclude that conventional electronic structure theory works very well for these two monoxides PdO and PtO. Both the nonmagnetic as well as the semiconducting properties are well ac-

counted for. Thus it is clear that the electronic structure of PdO and PtO is much more simple than the electronic structure of NiO. This also suggests that the most stable hypothetical nonmagnetic structure of NiO is likely to be found for the same geometrical structure as PdO and PtO. If NiO under very high pressure will undergo a metallization, it is not unreasonable that this would be accompanied by a crystallographic change from the sodium chloride structure into the present tetragonal structure, and thereby possibly NiO might aviod the metallic state in favor of a semiconducting but nonmagnetic behavior.

ACKNOWLEDGMENTS

We wish to acknowledge T. Gasche for valuable discussions. One of us (S.A.) would like to thank the Condensed Matter Theory Group at Uppsala University for their kind hospitality.

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