PHYSICAL REVIEW B VOLUME 44, NUMBER 3 15 JULY 1991-I

# Intermediate coupling in $L_2$-$L_3$ core excitons of MgO, $Al_2O_3$, and $SiO_2$

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(Received 20 December 1990; revised manuscript received 15 February 1991)

The $L_{23}$ reflection spectra for single-crystal MgO, $\alpha$-$Al_2O_3$, and $\alpha$-$SiO_2$ are measured. These reflection spectra are used to generate absorption spectra that agree well with electron-total-yield and electron-energy-loss measurements. Exciton features are shown to exist in the band gap by comparing the valence-band maximum plus optical band gap to the observed transition energies. The energy splitting of the $L_2$-$L_3$ excitons, as seen in reflection, is clearly resolved for $Al_2O_3$ and $SiO_2$, while in electron-total-yield measurements the doublets are not resolved for $Al_2O_3$. This resolution allows the calculation of the exchange energy using intermediate-coupling theory.

Core-hole absorption spectroscopy, in the form of electron total yield (TY) or electron-energy-loss spectroscopy (EELS), has been widely used to probe the unoccupied states of solids. In general, an electron is excited from a core hole to an unoccupied state. The density of these unoccupied states is monitored either by continuously changing the incident photon energy (TY) or by monitoring the energy loss from an incident electron beam (EELS). The presence of the core hole in the final state often strongly affects the absorption spectra. In insulators[1-5] and in some semiconductors[5,6] the screening of the core hole is brought about by the formation of excitons that appear as intense features near the absorption threshold. In transition metals[7,8] and transition metal compounds[9-12] the core hole couples with the excited electron, resulting in nonstatistical ratios in the observed $L_3/L_2$ intensity ratio.

In this paper we present data on the $L_{23}$ absorption of single-crystal MgO, $\alpha$-$Al_2O_3$, and $\alpha$-$SiO_2$. These absorption measurements were obtained with soft-x-ray reflection spectroscopy, a technique not typically applied to this problem. In our analysis we show that excitons are created in the band gap for each of the samples studied. These excitons are due to $2p^6 \rightarrow 2p^5 3s^1$ transitions in the cations. The observed $L_3/L_2$ intensity ratio of these excitons is less than the statistical value of 2/1. The presence of the core hole thus strongly influences the $L_{23}$ absorption spectra of MgO, $Al_2O_3$, and $SiO_2$ near threshold.

Variations in the $L_3/L_2$ intensity ratio are discussed in terms of intermediate-coupling theory. Intermediate-coupling theory[13] is appropriate when the spin-orbit splitting ($\xi$) is comparable to the exchange energy ($\Delta$). For the excitations discussed in this paper, $\xi$ is the $L_{23}$ spin-orbit splitting of the cation and $\Delta$ is the exchange energy of the core hole and the excited electron that are bound in the exciton state.

When the $L_{23}$ spin-orbit splitting is much greater than the exchange energy, *jj* coupling is obeyed. In *jj* coupling the relative intensity ($L_3/L_2$) for an excitation of the type $p^6 \rightarrow p^5 s^1$ will have the statistical value of 2/1 and the observed energy separation will be equivalent to $\xi$. At the opposite extreme, $\Delta \gg \xi$, **LS** coupling is obeyed and only one transition is observed for an excitation of the type $p^6 \rightarrow p^5 s^1$, namely $^1S \rightarrow {}^1P$. Intermediate-coupling theory is needed for the range of values of $\Delta$ and $\xi$ for which one of these extremes is not fulfilled. Qualitatively, the intermediate-coupling theory predicts that as $\xi/\Delta$ becomes greater than zero the excitation $^1S \rightarrow {}^3P$ becomes allowed. The intensity of this transition is small compared to the **LS** allowed $^1S \rightarrow {}^1P$ transition and the energy separation is equivalent to $\Delta$. As $\xi/\Delta$ becomes larger this peak grows in relative intensity and eventually the statistical ratio is reached.

Onodera and Toyozawa[4] applied this model to the absorption spectra observed for alkali halides. Here the solid is assumed to be purely ionic and the excitations are calculated as in free ions. The first excited states are due to transitions of the type $p^6 \rightarrow p^5 s^1$. Onodera and Toyozawa,[4] in a theoretical analysis, showed that in the range of $\xi/\Delta > 1$ the observed energy splitting of the two peaks would remain relatively constant while the $L_3/L_2$ intensity ratio would vary appreciably. This suggested that a measure of the intensity ratio gives an estimate for the exchange energy in the solid if it is assumed that $\xi$ has the same value as in the free ion. Using this approach Onodera and Toyozawa determined the exchange energy for different alkali bromides.

Since Onodera and Toyozawa's work intermediate coupling has been used to explain the absorption spectra of a number of solids. Recently the theory has been expanded to include crystal-field effects,[8-12] and more than two-particle final states.[9-11] These efforts are necessary when interpreting $p \rightarrow d$ transitions since the $d$ levels are split by the crystal field of the solid and typically the final state contains more than one $d$ electron. With these additions the intermediate-coupling theory has been used to interpret the absorption spectra of transition metals[7,8] and transition-metal compounds.[9–12] For the work discussed in this paper, which involves light metal oxides with no filled *d* bands, Onodera and Toyozawa's theory[4] is used to calculate the exchange energy in the solid form from the observed $L_3/L_2$ intensity ratio. This is compared to the exchange energy for the free atoms as determined from spark fluorescence measurements.[14] No inclusion of crystal-field effects are necessary in this work since the excited electron is in an *s* state for each of the samples studied.

The refectivity and emission measurements were performed on beamline U10A (Ref. 15) at the National Synchrotron Light Source, Brookhaven National Laboratory. This is a dedicated soft-x-ray emission (SXE) beamline employing both photon- and electron-excited SXE capabilities. The spectrometer is a 5-m-radius toroidal grating with Rowland optics. For these experiments either a 600 l/mm grating or a 300 l/mm grating were used, the input slit was set at 40 $\mu$m corresponding to a resolution of $<0.1$ eV. For the emission experiments 500 or 1000 eV electrons were used. For the reflectivity measurements a small fraction, on the order of 1 mW, of the white light beam illuminated the samples at 15° off normal and the specularly reflected light was collected using the SXE spectrometer. For near normal incidence the refectivity goes as

$$R=[(n-1)^2+k^2]/[(n+1)^2+k^2] \ , \qquad (1)$$

where $n+ik$ is the complex index of refraction. For soft x rays we assume that $(n+1)^2 \gg k^2 \gg (n-1)^2$, thus the reflectivity follows $k^2$, or, within the same approximation, $R$ follows $\mathcal{E}_2^2$, where $\mathcal{E}_2$ is the imaginary part of the dielectric constant which is proportional to absorption. With this approximation we equate $R^{1/2}$ to the relative absorption.

We have also analyzed the reflection spectra with Kramers-Kronig (KK) techniques. The conjugate variables used when interpreting refection data are $\ln(r)$ and $\theta$ where the complex reflection is defined as $re^{-i\theta}$. While KK analysis of reflection data has been extensively used to determine valence-band optical properties, problems result when attempting to analyze soft-x-ray reflection data. Since $\ln(r)$ is not bound for any energy range and the absolute reflectivities are typically $<0.1\%$, high-energy extrapolations are critical. Furthermore, we measured only the relative reflection and not the absolute. The analysis involved varying both the high-energy extrapolation [both $E^{-n}$ and $\exp^{(-aE)}$ were used] and the normalization of our relative intensity to an absolute intensity. The known reflectivity at lower energies was used and sum rules were employed. This analysis did not yield any conclusive results. Examination of the results suggested that $k$ was typically larger than $(n-1)$ by a factor of 2 or more and since $k \ll 1$ the above assumption leading to our approximation $R^{1/2} \propto \mathcal{E}_2$ may not be unreasonable.

In Fig. 1 we compare our absorption measurement, $R^{1/2}$, with EELS (Ref. 1) and TY (Ref. 2) data of MgO, TY data of $\alpha$-$Al_2O_3$,[16] and TY data of $\alpha$-$SiO_2$.[16] For $\alpha$-$SiO_2$ the TY data was shifted by 0.2 eV to achieve the best comparison. The necessity of the shift was probably a result of different spectrometer calibrations. For background subtraction we fit the region below threshold with $E^{-n}$. The backgrounds were less than 50% of the exciton peak heights. We feel the similarities represented in

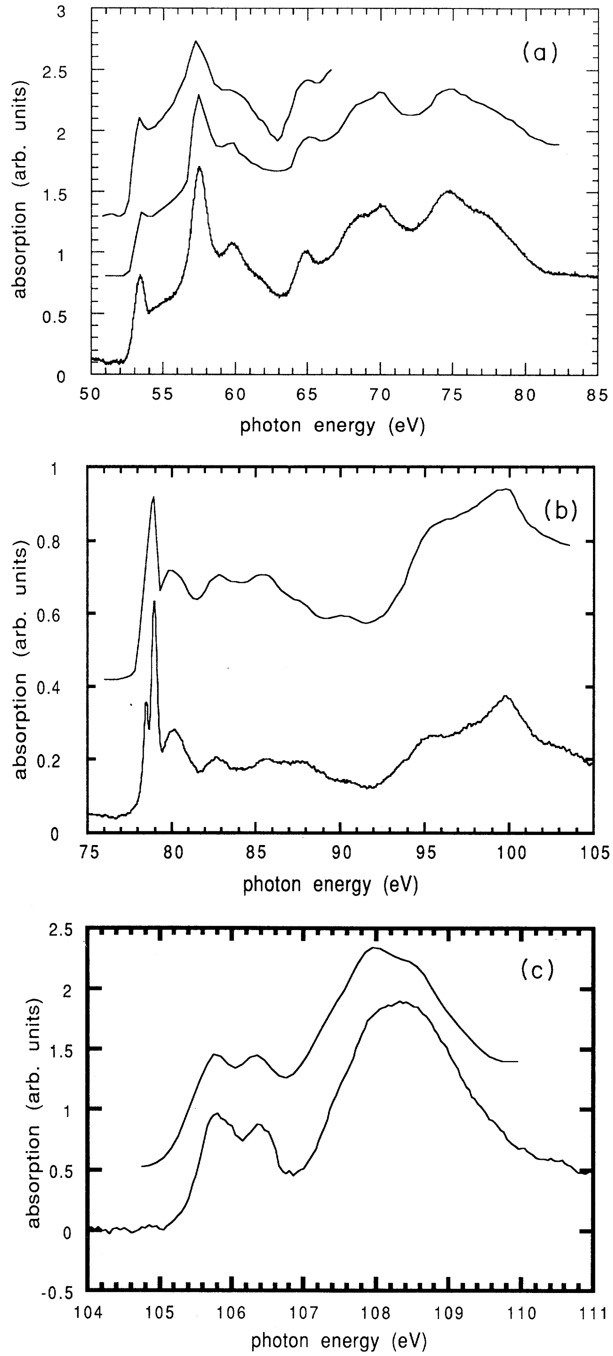

FIG. 1. (a) Comparison of the square root of reflection data, bottom, to EELS data (Ref. 1), middle, and TY data (Ref. 2), top, of MgO. TY and EELS data are offset for clarity. (b) Comparison of the square root of reflection data, bottom, to TY data (Ref. 16), top, of $\alpha$-$Al_2O_3$. TY data is offset for clarity. (c) Comparison of the square root of reflection data, bottom, to TY data (Ref. 16), top, of $\alpha$-$SiO_2$. TY data is offset for clarity.

Fig. 1 justify the use of our assumption, $(n+1)^2 \gg k^2 \gg (n-1)^2$. For $\alpha$-$Al_2O_3$ we obtain a sharp doublet near threshold while in TY work a broad peak is found. We feel this is due to sample charging, which does not affect our reflectivity measurements.

While the agreement of our absorption measurements with published TY measurements are good we feel it is necessary to discuss some of the problems associated with reflection measurements of this type. Since we are illuminating with white light, higher-order reflections must be considered. For $Al_2O_3$ the reflectivity at 160 eV is 5% of the background at 80 eV (near threshold). Furthermore the reflectivity is smooth here and would only affect an attempt at measuring the absolute reflectivity. The work presented here is limited to measurements of relative absorption and no attempt will be made to calculate absolute values of $\mathcal{E}_2$. The Al $L_1$ reflective features appear between 120 and 140 eV and do not affect the $L_{23}$ reflectivity in higher orders. The lowest-energy reflected light that would contribute structure to the Al $L_{23}$ reflectivity is fifth-, sixth-, and seventh-order O $K$ reflection. The intensity of these reflections, near 500 eV (O $K$), are negligible due to the 15° angle of incidence. The near normal incidence geometry acts as a higher-order filter. A similar argument can be made for $\alpha$-$SiO_2$ since here the $L_1$ structure appears between 150 and 180 eV and does not affect the $L_{23}$ spectra in higher orders. For MgO the $L_1$ structure is between 90 and 120 eV and would affect the $L_{23}$ structure if intense. We have investigated the $L_1$ reflection in first order and found its intensity to be $<5\%$ of the $L_{23}$ reflection intensity. We therefore assume any structure in the $L_{23}$ spectra due to second-order $L_1$ reflection negligible for MgO.

Another serious question regards the excitation depth for various photon energies. For $Al_2O_3$ we estimate that the penetration depth varies between 200 and 800 Å for the photon energy range used. This is due to the large changes in the extinction coefficient in this interval. Similar ranges in sampling depths are found for MgO and $SiO_2$. Therefore sample homogeneity is critical. The samples used were 500-μm-thick cut and polished single crystals, which were chemically cleaned before insertion into the vacuum. Surface smoothness is also critical. We found that the mirrorlike finishes obtained with mechanical polishing allow reflective measurements to be performed up to approximately 150 eV using the current experimental geometry.

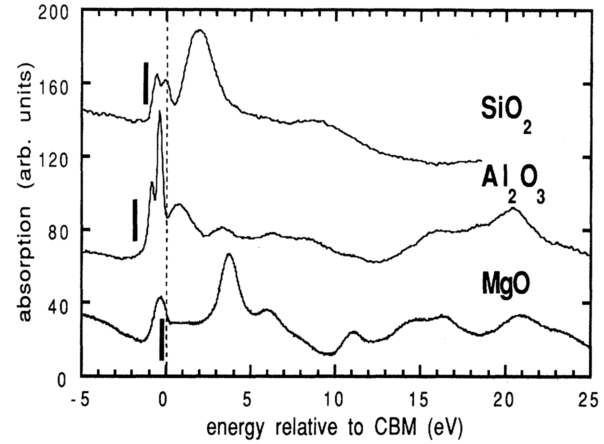

FIG. 2. Absorption spectra for MgO, $\alpha$-$Al_2O_3$, and $\alpha$-$SiO_2$ generated from reflection measurements. Spectra are shown relative to CBM as determined by our measurement of the VBM and the known optical band gaps. Also shown are the ${}^1S \rightarrow {}^1P$ transitions measured for the free atomic species $Mg^{2+}$, $Al^{3+}$, and $Si^{4+}$ (Ref. 14). Spectra are offset for clarity.

In Fig. 2 our absorption spectra, without background subtraction, are plotted relative to the conduction-band minimum (CBM). To determine the CBM the cation $L_{23}$ soft-x-ray emission spectra of each sample was obtained using electron beam excitation. These spectra were similar to those published in the literature.[2,16] The valence-band maximum (VBM), relative to the $L_3$ core hole, of each sample was determined from the SXE spectra, Table I. These values, together with the known optical band gap, were used to determine the CBM. Values used for the optical gap are 7.8 eV for MgO,[17] 9.5 eV for $\alpha$-$Al_2O_3$,[18] and 9.1 for $\alpha$-$SiO_2$.[19] Although recent values for the band gap of $\alpha$-$Al_2O_3$ vary between 9.5 and 9.9 eV, our choice of 9.5 eV does not affect any of the following discussion. Also shown in Fig. 2 are the first allowed excitations in the LS coupling scheme[14] for $Si^{4+}$, $Al^{3+}$, and $Mg^{2+}$ ions. These excitations are of the type $2p^6 \rightarrow 2p^5 3s^1$ and are the most intense excitations for the free ions in this energy region.

The excitations appearing below the CBM are core excitons, with the electron in an $s$-type atomic state. This is based on the comparisons with atomic excitation values, Fig. 2. These identifications have been made previously. For MgO the exciton excitation energy is almost identical, within 0.15 eV, to that of the first allowed excitation in $Mg^{2+}$. Similar results[20] are found in alkali halide ab-

TABLE I. Values for fitting parameters as described in the text. $E_{VBM}$ was obtained from a fit of the high-energy region in the $L_{23}$ SXE spectra. For the absorption fit $L_3/L_2$ is the relative intensity ratio, $\Delta E$ is the separation of the doublet, $E_{CBM}$ is the conduction-band minimum, and FWHM is the Gaussian broadening for MgO and $SiO_2$ and the Lorentzian broadening for $Al_2O_3$. The optical band gap, Refs. 17–19, compares well with $E_{VBM} - E_{CBM}$. All energies are given in eV.

| | $E_{VBM}$ | $E_{CBM}$ | Gap | $L_3/L_2$ | $\Delta E$ | FWHM |
|---|---|---|---|---|---|---|
| MgO | 45.95 | 53.72 | 7.8 | 0.1–0.3 | 0.276 | 0.8±0.1 |
| $Al_2O_3$ | 69.84 | 79.10 | 9.5 | 0.44 | 0.49 | 0.31 |
| $SiO_2$ | 97.3 | 106.73 | 9.1 | 1.1 | 0.61 | 0.56 |

sorption measurements and are predicted by the highly ionic character of these solids. For $Al_2O_3$ and $SiO_2$ the covalent character of the solid screens the exciton state effectively increasing its transition energy relative to that of the free ion. This screening also reduces the exchange energy, which results in the observed doublet structure.

To calculate the exchange energy the near threshold structure was analyzed using Onodera and Toyozawa's formalism. An $E^{-n}$ background was subtracted from each of the spectra. This background is due to contributions to $\mathcal{E}_2$ from valence excitations. The value of $n$ was determined from fitting the absorption spectra below threshold. Two Gaussians of variable intensity and position were used to describe the MgO and $\alpha$-$SiO_2$ excitons. The widths of these Gaussians were allowed to vary but not independently. For MgO the relative position of the two Gaussians was fixed at $\xi$. The structure at energies just above the excitons was fitted using $(E-E_{\rm CBM})^{1/2}$, since both band structure and cluster calculations show that states lying near the CBM are predominantly metal 3*s*. This was convoluted with a Gaussian with the same width as that used for the excitons. For $Al_2O_3$ a better fit was obtained using a Lorentzian line shape for the exciton. Figure 3 shows the fits obtained. The uncertainty in the relative intensity ratio for MgO was much larger than for the other oxides due to the small energy splitting and broader peaks. Values obtained from the fits are given in Table I together with our determination of $E_{\rm VBM}$ and the optical gap values reported in the literature. Our absolute accuracy in energy is estimated at 0.1 eV while the relative accuracy is estimated to be 0.03 eV. This is a result of using the same spectrometer for the measurement of the VBM and the absorption.

Comparison of the optical gap with $E_{\rm CBM}-E_{\rm VBM}$ suggests that we are indeed fitting the bottom of the conduction band. We have previously reported[21] soft-x-ray emission spectra from $SiO_2$ and $Al_2O_3$ that shows emission not only from the exciton levels, but also from states near the bottom of the conduction band. This indicates that both absorption and emission in these core-excited atoms near the $L_{23}$ threshold are associated with transitions to or from states localized by the core hole. Therefore, the absorption just above the optical gap has both ground-state character [they are fit reasonably well with $(E-E_{\rm CBM})^{1/2}$] and character due to the presence of the core hole.

The instrumental resolution was $<0.1$ eV in the energy range for each of the excitons. The excess broadening, Table I, is due to either strong phonon coupling, band dispersion, or exciton lifetimes. The lifetime of the core holes in question are governed by Auger decay rates. The excited electron is trapped by the core hole and does not have enough energy to disperse into the conduction band. Furthermore, our SXE results[21] show that the direct radiative recombination of the core exciton is much less probable than radiative recombination of the core from valence electrons. Therefore the lifetime of the exciton should be very similar to the lifetime of the core hole, which is tens of meV, much less than the broadenings measured.

Excess broadening for $p \rightarrow d$ transitions in transition-metal compounds has been observed by de Groot *et al.*[12] and has been attributed to phonon coupling. The broadening was shown to increase with a decrease in interatomic distance. This comparison is meaningful only between samples of the same crystalline structure and similar dielectric properties and therefore no such com-

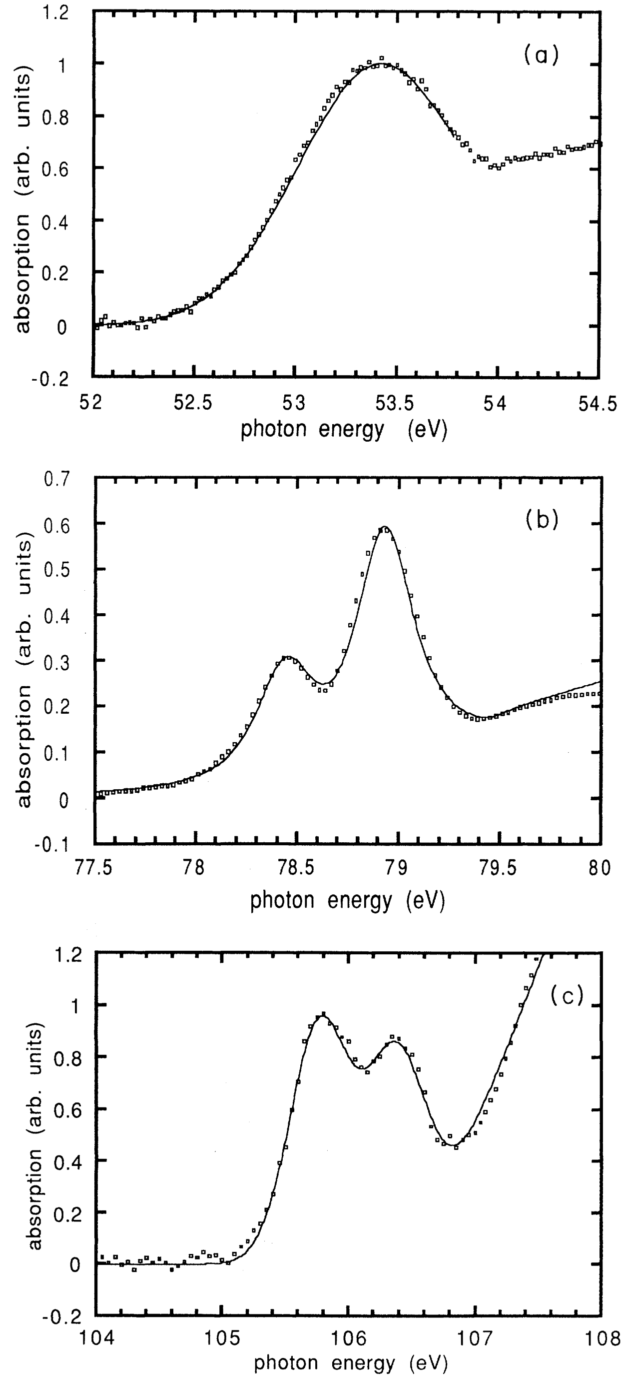

FIG. 3. (a) Fit to MgO absorption near threshold. (b) Fit to $\alpha$-$Al_2O_3$ absorption near threshold. (c) Fit to $\alpha$-$SiO_2$ absorption near threshold.

parison will be made to our results. Phonon coupling for ionic compounds with the same crystalline structure as MgO is typically large.[22] Full width at half maximum (FWHM) broadenings of 1 eV have been reported at room temperature in x-ray photoemission spectroscopy (XPS). It should be noted that the final state in these XPS measurements is different than in ours. It is interesting that the exciton line shape for MgO and $SiO_2$ are Gaussian and for $Al_2O_3$ Lorentzian. Toyozawa[23] has shown that Lorentzian line shapes are expected for weak phonon coupling and that Gaussian line shapes are expected for strong phonon coupling. To more fully understand this broadening we are beginning line-shape measurements as a function of temperature for these oxides. We are unable at this time to discuss the band-structure effects on the broadening.

The exchange energy is calculated from the observed intensity ratio using the Onodera model. In this model the intensity ratio is

$$L_3/L_2=\tan^2[\arctan 2^{1/2}-\tfrac{1}{2}\arctan 8^{1/2}\Delta/(3\xi-\Delta)]\ . \tag{2}$$

Here we vary $\Delta$, holding $\xi$ constant at the atomic value. The results are given in Table II together with atomic values calculated from Ref. 14 using the atomic result[13]

$$\Delta E=(\Delta^2-\tfrac{2}{3}\xi\Delta+\xi^2)^{1/2}\ , \tag{3}$$

where $\Delta E$ is the observed energy splitting between the $^1P$ and $^3P$ final states of the free ion.[14]

The results in Table II show that the reduction in exchange energy in going from the free ion to the oxide decreases in the order $SiO_2 > Al_2O_3 > MgO$. One effect in going to the solid state that reduces the exchange energy is screening. Screening of the core hole would increase the physical size of the exciton, thereby decreasing the exchange energy. In an extreme case, infinite separation of core hole and excited electron, the exchange energy would be zero and *jj* coupling obeyed. The relative screening for the three oxides can be estimated by comparing calculated electron densities near the cations in the solid. While many such calculations exist in the literature, comparison is difficult due to the arbitrary manner in which "near the cations" is interpreted. For this reason we quote the results of Tossell[24] who has calculated the charge in a sphere around the cations in the $SiO_6^{-8}$, $AlO_6^{-9}$, and $MgO_6^{-10}$ clusters in a consistent manner. The results of these calculations, $Z^*$, are given in Table II along with the charge $Z$ of the free ion used for comparison. Although the absolute magnitude of these values has no significant meaning the trend should be correct and does follow what is expected from the relative electronegativities of the metal atoms. The values of $Z^*/Z$ show that screening of the metal ions increase in the order $MgO < Al_2O_3 < SiO_2$. This is consistent with our results based on the above argument.

TABLE II. The spin-orbit splitting $\xi$, and the atomic exchange energy in the free ions, $Mg^{2+}$, $Al^{3+}$, and $Si^{4+}$, as determined from Ref. 14. The exchange energy in the solid is determined from the absorption data and (2). The solid-state effects on the exchange energy are discussed in terms of the screening. $Z^*/Z$, where $Z^*$ is the cation charge in the solid and $Z$ is the charge in the free ion. The cluster calculations of Ref. 24 were used for values of $Z^*$.

| | $\xi$ (eV) | $\Delta_{\text{atomic}}$ (eV) | $\Delta_{\text{solid}}$ (eV) | $Z^*/Z$ |
|---|---|---|---|---|
| MgO | 0.276 | 0.608 | 0.25–0.5 | $1.8/2=0.9$ |
| $Al_2O_3$ | 0.426 | 0.804 | 0.31 | $2.5/3=0.8$ |
| $SiO_2$ | 0.632 | 0.987 | 0.18 | $2.8/4=0.7$ |

We have demonstrated the usefulness of doing white light reflectivity measurements using monochromatic detection as an alternate means of measuring the absorption spectra. The reduction in the exchange energy in going from free ion to oxide was determined for MgO, $Al_2O_3$, and $SiO_2$. These reductions in $\Delta$ were explained in terms of screening in the solid state. With the advent of third-generation synchrotron sources photon-excited SXE will become a more useful research tool. Together with this, the complementary absorption measurements of the type discussed in this paper should receive increased attention. Both techniques, photon-excited SXE and near normal incidence soft-x-ray reflectivity, probe the solid down to hundreds of angstroms as opposed to the more surface sensitive techniques of ultraviolet photoemission spectroscopy and XPS.

This work was supported by the National Science Foundation under Grant No. DMR-8715430, and the National Institute of Standards and Technology.

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