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Influence of magnetic ordering on the NiO valence band

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The influence of magnetic ordering on the NiO valence band has been studied by angle resolved photoelectron spectroscopy. Measurements have been performed at temperatures above and below the Néel temperature (T_N), as well as at room temperature. The results show temperature dependence but no significant changes in the valence band structure are detected in connection to the passing of T_N . The reported data suggest that the magnetic phase transition does not influence the valence band structure significantly.

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The controversy concerning the best way to theoretically describe systems with strong correlation, such as NiO, is an old one. In 1949 Mott¹ presented his theory to explain why NiO and other related compounds are insulators and not conductors as expected by a valence count (crystal field splitting included). In the 1960s Hubbard introduced a more elaborate model² for the localization of d electrons as a result of intra-atomic repulsion. Since this time, significant progress has been made in incorporating correlation effects into band structure calculations. Most current band structure calculations are based on density functional theory³ and make use of the local density approximation or its spin resolved equivalent (LSDA).⁴ These calculations give good quantitative agreement with experiments for many materials but in the case of transition metal oxides the agreement is not satisfactory.⁵ The calculations often include the fact that the transition metal oxides, as NiO and others, are magnetically ordered, and predict drastic changes in the band structure at the magnetic phase transition. This makes it highly interesting to perform photoemission experiments on NiO above and below the Néel temperature (T_N) in order to investigate the effect of the magnetic ordering on the electronic structure. Angle resolved photoemission data from such an investigation are presented in this report and it is shown that the magnetic phase transition induces no significant changes in

the measured photoelectron (PE) spectra. This result has two possible explanations. One is that local magnetic ordering persists above the transition temperature and the other is that the magnetic ordering has no or little effect on the electronic structure. Temperature effects presumably not related to the magnetic ordering are observed and discussed in the framework of a Gaussian temperature broadening.

The measurements were performed at the national synchrotron radiation facility Max-lab in Lund Sweden, at beamline (BL) 41.⁶ This BL is equipped with a toroidal grating monochromator and a hemispherical electron energy analyzer, with an acceptance angle of $\pm 1^\circ$. All results were obtained from an *in situ* cleaved NiO single crystal measured in normal emission. The crystal was cleaved at a pressure of $\sim 10^{-9}$ torr and then transferred into the analysis chamber where the base pressure was $\sim 3 \times 10^{-10}$ torr. The surface quality was checked by low energy electron diffraction (LEED). Observed LEED patterns showed sharp 1×1 spots. A tantalum film spot welded to the sample holder was used to determine the Fermi edge and the total energy resolution which was found to be ~ 0.3 eV. The sample was heated by means of a resistive coil mounted directly behind the sample holder. The temperature was controlled by a thermocouple mounted on the side of the sample holder and the temperatures quoted below are those measured by the thermocouple.

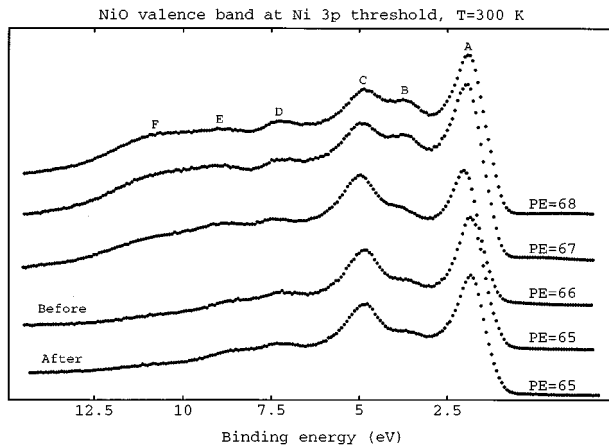


FIG. 1. Normal emission spectra of the NiO valence band at photon energies corresponding to the Ni $3p$ absorption edge. The spectra were recorded at a temperature of 300 K. At the bottom of the figure, a comparison, between spectra recorded before and after heating, is made.

Since NiO starts to sublime at its T_N (Refs. 7 and 8) 525 K, the measurements at elevated temperatures had to be performed as quickly as possible. In order to reduce the measuring time, no energy calibration spectra were taken at temperatures above room temperature. That no important surface deterioration took place can be seen in Fig. 1, where the two spectra at the bottom show the NiO valence band at 65 eV PE before and after the measurement series. It is seen that all structures are the same before and after, and that there are no significant variations in intensity. This fact is important since it excludes the possibility of artifacts in the temperature dependent spectra.

Measurements were performed at three different temperatures: room temperature (300 K), 500 K, and 615 K. These temperatures were chosen so that any changes due to the magnetic phase transition at 525 K could be sorted out from other temperature dependence. At 500 K the correlation length is still in the order of 100 Å or more, as seen by neutron diffraction, but 615 K is well above T_N and not even short range order exists.⁸ At each temperature, spectra at 65, 66, 67, and 68 eV PE were recorded. These photon energies correspond to the Ni $3p$ absorption threshold [~ 66 eV PE (Ref. 9)] and are therefore especially suited for this kind of investigation by exploiting resonant photoemission from the valence band. In the resonant process, two different photoemission channels are open, which can interfere to give an enhanced probability of emission. The first channel is the direct photoemission channel and the second one is in this case the photoexcitation of a Ni $3p$ electron into an empty Ni $3d$ state followed by an autoionization. The second channel requires that the intermediate state is localized and a resonant feature in the valence band is thus Ni related and indicates the presence of localized excited Ni states. It has already been shown that this happens in NiO at the Ni $3p$ absorption threshold⁹⁻¹¹ and it is also seen in the spectra displayed in Fig. 1, where the enhancement of the feature labeled *F* is especially evident. The enhancement of feature *C* can also be seen while a more detailed analysis is needed to show that the entire valence band including feature *A* is resonating at

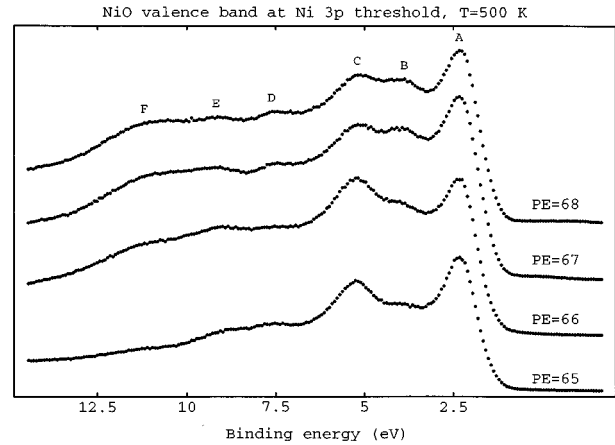


FIG. 2. Normal emission spectra of the NiO valence band at photon energies corresponding to the Ni $3p$ absorption edge. The spectra were recorded at a temperature of 500 K.

the threshold. This is discussed further below.

It has been shown that the oxygen related bands, which are the ones expected to be modified by the phase transition, coincide with experimental data if the final state is modeled as a free electron like state with an inner potential of ~ -7 eV.^{5,12} In this framework a PE of ~ 67 eV corresponds to a k_{\perp} of approximately 0.7–0.8 in units of π/a for binding energies (BE's) between 3 and 7 eV. At this point in the Brillouin zone there are according to calculations¹² three bands situated at approximately 3.5, 4.5, and 7 eV BE, respectively, in the paramagnetic case and in the antiferromagnetic case there is also a band at 5.5 eV. At the phase transition from antiferromagnetic to paramagnetic this band should thus vanish according to the LSDA calculation. Since the 5.5 eV band is clearly separated from the other bands, this PE gives every opportunity to detect the proposed change in band structure related to the magnetic phase transition.

In Fig. 1, spectra recorded at room temperature (300 K) are displayed. There are six clearly visible features seen in each spectra, labeled *A* through *F*. The most intense peak, *A*, is seen at ~ 2 eV BE followed by a weaker peak *B* at ~ 3.5 eV BE. At ~ 5 eV BE a second intense peak *C* appears, which is then followed by a low intensity peak *D* at ~ 7.5 eV BE and *E* at ~ 9 eV BE. For PE's higher than 65 eV there is also a feature at ~ 11 eV BE labeled *F*. The two peaks *E* and *F* have previously been attributed to a Ni d^7 final state.^{12,13} When the PE is increased from 65 eV it is seen that the *E* and *F* peaks are enhanced, especially peak *F*, as mentioned above, which is hardly visible at 65 eV PE. This enhancement indicates states of Ni character in agreement with the Ni d^7 labeling. At 67 and 68 eV PE, peak *B* is also strongly enhanced and a more detailed study shows that the features *A*, *C*, and *D* also increase in intensity at the threshold. A detailed analysis as well as experimental studies of this resonance have been presented elsewhere^{9-11,14} and will not be repeated here.

In Fig. 2, the valence band spectra displayed are recorded at 500 K. It is clear that the same features are present here as in the spectra recorded at room temperature. There are however some differences between the spectra of Figs. 1 and 2.

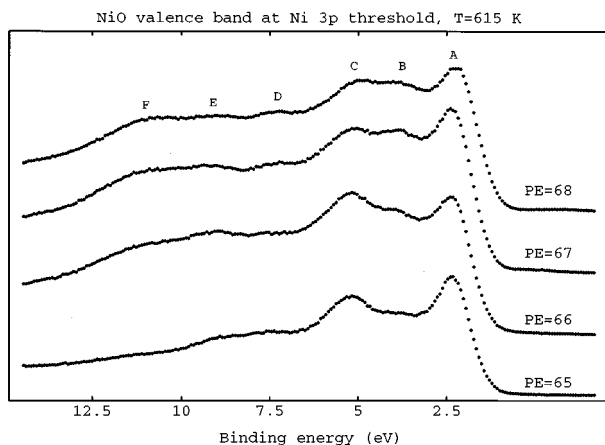


FIG. 3. Normal emission spectra of the NiO valence band at photon energies corresponding to the Ni $3p$ absorption edge. The spectra were recorded at a temperature of 615 K.

The relative intensity of peaks A and C is lower than at 300 K. The peaks are also broader at higher temperature as can be expected. Furthermore, the peak to peak distance between peaks A and C decreases slightly in the order of 100 meV. There is, however, no change seen in the behavior of the resonance. Features B and F are still most strongly enhanced with weaker enhancements seen in A, C, D, and E.

As indicated above, the number of observed features is expected to decrease according to LSDA calculations when the temperature is increased above 525 K. Valence band spectra of NiO at 615 K are presented in Fig. 3. Already from a first glance, it is evident that no dramatic changes are seen as compared to the spectra at 300 K and 500 K. The number of features is the same as well as the approximate BE's. The relative intensity of peaks A and C continue to decrease, the peaks broaden even further and the peak to peak distance is even smaller than at 500 K. A comparison with the spectra taken below T_N indicates that there is no difference in the behavior of the resonance below and above T_N .

In order to investigate the temperature effects more quantitatively, the valence band measured at 300 K has been broadened, to account for temperature changes, and fitted to the data collected at 500 K and 615 K. The result is given in Fig. 4. The valence band spectra for 65 eV PE at different temperatures have been normalized to equal the total area. The 300 K valence band spectrum was then convoluted with a Gaussian and fitted to the 500 K and 615 K spectra. A Gaussian was chosen as the convolution function to simulate the different contributions to the thermal broadening. At the bottom of Fig. 4, the comparison with the 500 K spectrum is shown. The continuous and broken lines represent a broadening of the 300 K spectrum with a 0.55 and 0.35 eV full width at half maximum (FWHM) Gaussian, respectively. The quoted values are those which give the best fit to the valence band edge as judged by eye. A least squares fit is of no use in this case since temperature effects other than broadening are present. The relatively large uncertainty in the fit does not influence the qualitative effects described below. It is clearly seen that the Gaussian broadening is not sufficient to explain the induced changes. Spectral weight is

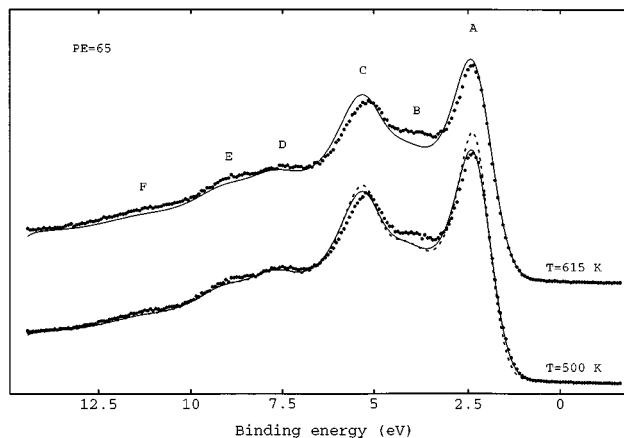


FIG. 4. The 300 K spectrum convoluted with a Gaussian and fitted to the 500 K and 615 K spectra.

transferred from peaks A and C to peak B and possibly to higher BE parts of the valence band. A small “compression” of the valence band is also observed, i.e., the peak to peak distances decrease. The top of Fig. 4 displays the fit of the convoluted 300 K spectrum to the 615 K spectrum. Here, the Gaussian used for the convolution has a FWHM of 0.7 eV. The broadening width scales approximately linearly with temperature as can be expected from sudden approximation arguments.¹⁵ Discrepancies seen between the convoluted 300 K spectrum and the 500 K spectrum are seen even more clearly in the case of the 615 K spectrum. More spectral intensity is transferred from peaks A and C to peak B and the high BE parts of the valence band. The decrease in peak to peak distances is now even larger and clearly seen for all valence band features. A possible factor, in this “compression” of the valence band is anharmonic effects, i.e., lattice expansion. The spectral weight transfer could possibly be ascribed to a wave vector dependence in the Debye-Waller factor. It has been shown experimentally¹⁶ as well as in model calculations¹⁷ that the Debye-Waller factor can depend on the wave vector and that the decrease in intensity can differ between spectral features, hence leading to apparent spectral weight transfer, but detailed theory would be needed to confirm this, something which will not be attempted in the present context.

The redistribution of intensity and the reduction of peak to peak distance is only continued as the temperature is increased from 500 K to 615 K. It is also clear that the resonance at 615 K is similar in nature to that at 500 K. One can therefore conclude that even though there are temperature effects present there are no indications of any significant changes in the valence band spectra related to the passing of the Néel point. A possible explanation for this is that the influence of antiferromagnetic ordering on the valence band structure is very weak. Another possibility is that of local magnetic ordering persisting even above T_N as in MnO (Ref. 18) and KMnF_3 .¹⁹ It does, however seem unlikely that any strong correlation persists since magnetic neutron scattering shows no diffuse scattering above T_N .⁸ The lack of changes in the valence band structure related to the magnetic phase transition thus indicates that the change of magnetic ordering has no dramatic effect on the valence band structure.

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