¹¹R. L. Martin and E. R. Davidson, Phys. Rev. A <u>16</u>, 1341 (1977).

¹²M. Mehta, C. S. Fadley, and P. S. Bagus, Chem. Phys. Lett. <u>37</u>, 454 (1976); T. A. Carlson, Phys. Rev. 131, 676 (1963). ¹³T. A. Carlson and M. V. Krause, Phys. Rev. <u>140</u>, A1057 (1965); V. Schmidt, N. Sandner, H. Kuntzemuller, P. Dhez, F. Wuilleumier, and E. Kallne, Phys. Rev. A <u>13</u>, 1748 (1976); D. M. P. Holland, K. Codling, J. B. West, and G. V. Marr, to be published.

Dispersion and Symmetry of Oxygen-Induced Bands on A1(111)

W. Eberhardt

Department of Physics and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

and

F. J. Himpsel

Synchrotron Radiation Center, University of Wisconsin-Madison, Stoughton, Wisconsin 53589 (Received 4 December 1978)

Using polarized light and angle-resolved photoelectron spectroscopy, we have shown that oxygen is bonded in an ordered (1×1) configuration on Al(111). For this model system, we have determined the symmetry and dispersion of the three oxygen derived bands. We find two even and one odd band with respect to the $(1\overline{10})$ mirror plane. A disordered oxide film shows no dispersion and different oxygen binding energies.

Oxygen adsorbed on Al is theoretically one of the simplest adsorption systems. There are no d bands in the metal to complicate the calculation, so that the bonding is s-p in nature. As a consequence, several ab initio calculations exist for this system $^{1-4}$ and different theoretical approaches can be compared. Experimentally, this system has proven to be much more difficult because of the formation of an oxide layer instead of a chemisorbed monolayer. We report in this Letter the first observations of the two-dimensional band dispersion of a chemisorbed layer of oxygen on Al(111). These data will furnish a definitive test for *ab initio* calculations for oxygen bonding on Al and can, in fact, be used to distinguish bonding sites.

A few groups have studied the oxidation of Al single crystals. Work-function changes, ^{5,6} angle-integrated photoemission valence-band spectra, and Al 2p core-level spectra have been reported. ^{7,8} From these studies, the oxygen on Al(111) would seem to be the most profitable to study since it appears to form an ordered overlayer during the initial stages of adsorption. Flod-ström *et al.*⁷ found that the (1×1) low-energy-electron-diffraction (LEED) pattern from Al(111) changed only in intensity during the initial stages of oxygen adsorption. This could be interpreted as indicating the formation of an (1×1) ordered overlayer. Our angle-resolved photoelectron spectra show

that the oxygen levels in this coverage range exhibit the symmetry and dispersion expected from a (1×1) ordered overlayer. Specifically, we find three oxygen-2*p*-derived bands in the (110) mirror plane, one odd and two even with respect to reflection about the mirror plane. The largest dispersion (~2.7 eV) is observed for the oxygen p_x, p_y -derived bands. Our results show that the dispersion is mainly determined by the oxygen-substrate-oxygen interaction via the p_x, y orbitals. This favors the threefold hollow position. Also, the periodicity of the dispersion proves the oxygen unit cell has the same dimension as the surface unit cell; i.e., we have an ordered (1×1) overlayer.

The experiments were performed at the Synchrotron Radiation Center of the University of Wisconsin. We used two different spectrometers. One was a two-dimensional-display spectrometer.⁹ *P*-polarized light with an angle of incidence of 55° was used in the photon energy range 12 eV $\leq h\nu \leq 35$ eV. The second system was a 180°-deflection-type analyzer¹⁰ which is fully rotatable about two orthogonal axes. The polarization of the incident light is continually variable, allowing us to separate orbitals of different symmetry.

The Al(111) surface was prepared by sputteringannealing cycles with Ne ions. The surface was characterized and oriented *in situ* by LEED and photoelectron spectroscopy. The cleanliness of

the sample was checked by photoemission. Thus, oxygen contaminations of much less than 1% of a monolayer may be detected easily.⁸ Our clean spectra show that the remaining oxygen contamination, if any, is certainly well below an equivalent of 0.1 L (1 langmuir = 10^{-6} Torr sec) exposure with O_2 (0.001 monolayer¹¹). We exposed our surfaces to 4-24 L of O_2 activated by an ion gauge, i.e., a submonolayer coverage. We work in the submonolayer regime since for higher oxygen exposures a mixed system consisting of a chemisorbed oxygen overlayer and bulk oxide is formed.⁷ The work function increases by 0.10 ± 0.05 eV upon the overlayer formation after exposure to 24 L O_2 . This value is measured by taking the width of the energy distribution curve and is in agreement with previous results⁵ measuring the onset of the photoelectric yield but contradictory to the results obtained with the Kelvin probe.6

Figure 1 shows a typical set of angle-resolved energy distributions. The collection was at 30° from the normal which was chosen to give a k_{\parallel} near the zone boundary in the (110) mirror plane. The solid curve is for the polarization vector in the mirror plane so that only even initial states can be detected in the mirror plane. The dashed curve has the polarization perpendicular to the mirror plane of detection. Therefore, only odd initial states are seen. This holds because the



FIG. 1. Angle-resolved photoelectron energy distribution curves showing the odd (dashed curve) and even (full circle) oxygen-induced states. The detector was set at an emission angle of 30° away from the normal in the (110) mirror plane, corresponding for the oxygen-induced features in a k_{\parallel} which corresponds approximately to point M of the surface Brillouin zone. Odd states are selected by the electrical field vector \vec{E} perpendicular to the (110) plane, and even states by \vec{E} in the (110) plane.

matrix element is invariant under reflection about the mirror plane. We see two even states and one odd state. This behavior is expected for an ordered overlayer of oxygen. The p_z level forms one even band and the p_x, p_y levels form two bands, one odd and the other even with respect to the mirror plane. The energy position of these bands were measured as a function of k_{\parallel} , both by changing the collection angle and the photon energy.

Figure 2 shows the measured energy dispersion of the oxygen bands in the (110) mirror plane (see inset). The E vs k_{\parallel} dispersion shown in Fig. 2 is symmetric about $k_{\parallel} \simeq 1.27$ Å⁻¹ which is the Al(111) zone edge. Therefore, the oxygen unit cell is identical to the Al(111) unit cell. In the range between 4 and 24 L, we do not observe any coverage-dependent changes of the dispersion. Therefore, we conclude that the oxygen chemisorbs in the form of islands on the Al(111) surface, which explains the observation of dispersion even in the submonolayer regime. The p_z state has the lowest binding energy and smallest dispersion. The $p_{x,y}$ states are degenerate at I for symmetry reasons but not at M. The $p_{x,y}$ band which has even symmetry relative to the $\Gamma - M$ axis has the higher binding energy. The binding energy of the $p_{x,y}$ bands at Γ is given by the binding energy at $k_{\parallel} = 2.54 \text{ Å}^{-1}$ since this point corresponds to the Γ point in the second zone. Influenced by theoretical considerations, we have drawn the dispersion curve for the even $p_{x,y}$ band to match the energetic value of the odd $p_{x,y}$ band



FIG. 2. Experimental energy-vs- k_{\parallel} dispersions of the chemisorbed oxygen overlayer states. The upper band is p_z -like; the lower two bands are p_x, p_y which have to be degenerate at Γ . The inset shows the surface Brillouin zone.

at Γ . The photoemission at $\Gamma (k_{\parallel} = 0)$ results in one broad asymmetric peak [2.5 eV full width at half maximum (FWHM)], which can be resolved by curve fitting into two Lorentzians centered at $E_i = -6.7 \text{ eV} (p_z)$ and at $E_i = -7.7 \text{ eV} (p_{x,y})$. This is within the error limits in good agreement with the independently measured value for the Γ point of the second zone, where we observe only emission of the odd component. Our results are summarized in Table I.

A calculation which deals with the lateral interaction between the oxygen atoms only would result in a higher binding energy for the p_z level than for the $p_{x,y}$ levels at Γ . This was verified for a geometry fitting to a (100) plane earlier.^{3, 12} The interaction with the substrate affects mostly the $p_{x,y}$ orbitals³ and increases their binding energy and dispersion. This very effect is here experimentally observed for the (111) surface. The degenerate $p_{x,y}$ orbitals have a higher binding energy at Γ than the p_z orbital. Moreover, the p_z band disperses much less (~0.2 eV) than the $p_{x,y}$ bands ($\sim 2.7 \text{ eV}$). The width of the levels as observed in the photoemission is 2.5 eV (FWHM) for the even and 3.0 eV (FWHM) for the odd $p_{x,y}$ band, much larger than the 1.25 eV (FWHM) for the p_z band. The lifetime of a hole in the $p_{x,y}$ orbitals is apparently by a factor of 2 shorter than in the p_s orbital, which also indicates a much stronger interaction with the substrate for the $p_{x,y}$ orbitals. This clearly favors a threefold hollow site for the oxygen on Al(111). According to jellium calculations,¹ the energetic position of the oxygen 2p resonance and its shape is very sensitive to the vertical distance of the oxygen atoms from the surface plane. The observed oxygen binding energies and the small increase of the work function indicate a position outside but very close to the surface plane.⁷

Figure 3 shows angle-integrated photoelectron spectra in the valence-band region. These spectra characterize two different oxidation states of Al(111). The oxygen layer chemisorbed at room temperature shows an O-2p-induced peak cen-

TABLE I. Oxygen band energies at critical points of the surface Brillouin zone (in eV relative to E_F).

	Γ	М	
p_z $p_{x,y}$	-6.7 ± 0.2 -7.3 ± 0.3	$-6.5 \pm 0.2 \\ -8.1 \pm 0.3 \\ -9.4 \pm 0.5$	

tered at an initial-state energy $E_i = -6.7$ eV with a clearly pronounced shoulder at $E_i = -9.4$ eV with respect to the Fermi energy E_F . After heating the sample to about 800 K, the second oxidation phase is formed where the leading peak is shifted to $E_i = -7.25$ eV and the shoulder is not clearly visible any more but gives a continuum of states down to $E_i = -13.5$ eV. As in Ref. 7, we find for the chemisorbed overlayer a chemical shift of about -1.4 eV for the Al 2*p* levels and for the heated sample a chemical shift of -2.7 eV as it is observed for Al₂O₂.

In angle-resolved photoemission, we observe no dispersion of the oxygen levels with k_{\parallel} for the second oxidation phase. Also, polarization effects are absent. This is characteristic for a disordered phase.

In summary, we can distinguish clearly between two different states of oxygen on Al(111). The initial oxidation state forms an ordered (1×1) overlayer and has two-dimensional bandlike O 2p states, whereas after thermal reaction we find a disordered O-Al system. The ordered overlayer provides the first adsorbate system where two-dimensional band dispersion is observed and symmetry assignments can be made using strict polarization selection rules.

We would like to thank Professor E. W. Plummer and Professor P. Soven for many helpful and stimulating discussions as well as the staff of the Synchrotron Radiation Center for their excellent support. This work was supported by the National Science Foundation Materials Research Laboratories Program under Grants No.



FIG. 3. Angle-integrated photoelectron energy distribution curves for the clean Al(111) surface after exposure to oxygen at room temperature, and after annealing of the oxygen layer to ~ 800 K.

DMR 76-00678 and No. DMR 77-21888.

¹N. D. Lang and A. R. Williams, Phys. Rev. Lett. <u>34</u>, 531 (1975), and Phys. Rev. B 18, 616 (1978).

²J. Harris and G. S. Painter, Phys. Rev. Lett. <u>36</u>, 151 (1976).

³I. P. Batra and S. Ciraci, Phys. Rev. Lett. <u>39</u>, 774 (1977).

⁴P. R. Salahub, M. Roche, and R. P. Messmer, Phys. Rev. B 18, 6495 (1978).

⁵P.O. Gartland, Surf. Sci. 62, 183 (1977).

⁶A. M. Bradshaw, P. Hofmann, and W. Wyrobisch, Surf. Sci. 68, 269 (1977); A. M. Bradshaw, private communication.

⁷S. A. Flodström, C. W. B. Martinsson, R. Z. Bachrach, S. B. M. Hagström, and R. S. Bauer, Phys. Rev. Lett. 40, 907 (1978).

⁸W. Eberhardt and C. Kunz, Surf. Sci. <u>75</u>, 709 (1978). ⁹D. E. Eastman, F. J. Himpsel, and J. J. Donelon,

Bull. Am. Phys. Soc. 23, 363 (1978).

 $^{10}\mathrm{C.}$ L. Allyn, T. Gustafsson, and E. W. Plummer, Rev. Sci. Instrum. $4\underline{9}$, 1197 (1978).

¹¹C. Martinsson, L. G. Petterson, S. A. Flodström, and S. B. M. Hagström, in Proceedings of the Conference on Photoemission from Surfaces, Nordwijk, Holland, 1976, European Space Agency, Neuilly-sur-Seine,

Report No. SP118 (unpublished), p. 177.

¹²A. Liebsch, Phys. Rev. Lett. <u>38</u>, 248 (1978), and Phys. Rev. B <u>17</u>, 1653 (1978).

Magnetic Ordering in Cerium Monochalcogenides: A Test Case for ϵ Expansions with n=4

H. R. Ott^(a) and J. K. Kjems Risø National Laboratory, DK-4000 Roskilde, Denmark

and

F. Hulliger

Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule–Hönggerberg, 8093 Zürich, Switzerland (Received 17 January 1979)

CeSe and CeTe are found by neutron diffraction to be type-II antiferromagnets with the moment along the propagation vector. The phase transitions are continuous with the critical exponent for the magnetization $\beta = 0.36 \pm 0.02$. This constitutes a violation of the ϵ -expansion predictions of Bak, Krinsky, and Mukamel, which hitherto have been successfully applied to a number of $n \ge 4$ systems and according to which the transitions should be of first order.

In recent developments of phase-transition theories the renormalization-group approach has been widely used and has given a formal background to the ideas of universality and scaling. Concomitantly the ϵ -expansion technique has been developed as a perturbation scheme to calculate universal quantities such as critical exponents from the renormalization-group equations. Using these concepts, Bak, Krinsky, and Mukamel in a series of papers¹ investigated the critical behavior of phase transitions where the order parameters involved have $n \ge 4$ components. As a main result of their investigation they found a phenomenological rule, supplementary to the Landau symmetry criteria, for phase transitions to be of first order. This new rule states that a phase transition is of first order when no stable fixed point can be found within the ϵ expansion. The rule can be applied when the

symmetry is known above and below the phase transition.

These authors also gave many examples of physical systems where order parameters have four or more components. These are metals and compounds undergoing magnetic phase transitions which lead to a doubling of the unit cell along one or more directions. In some cases the proposed rule was corroborated by existing experimental results^{2,3} (e.g., UO₂, MnO, Cr, Eu) and for other systems (mainly rare-earth pnictides and chalcogenides) the order of the magnetic phase transitions were predicted. One such class of materials is the Ce monochalcogenides CeS, CeSe, and CeTe. They crystallize in the cubic rocksalt structure and are all reported to undergo a magnetic phase transition at low temperatures.^{4,5} Schobinger-Papamentellos and coworkers⁶ determined the ordered phase of CeS