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Experimental and Theoretical Studies of Electron Binding Energies for Water Adsorbed on α-Alumina

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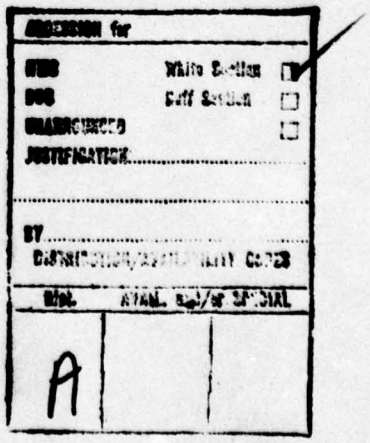

Abstract

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I. Introduction

The utility of ultraviolet photoelectron spectroscopy [1] (UPS) for the detailed analysis of adsorbant-adsorbate bonding has been widely recognized in the case of adsorption on metal surfaces [2], and the value of SCF-Xα-SW calculations [3,4] in the interpretation of these spectra has been repeatedly demonstrated [5]. In this paper we present both experimental and theoretical results for an insulator system, $Al_2O_3(0001)/H_2O$, of considerable intrinsic and practical interest. Our purpose is to compare, for an insulator, the experimental electron energy spectrum obtained by HeI irradiation with the spectrum predicted using the SCF-Xα-SW method and a small model cluster. We also are able to correlate our results with work of other kinds on less well-defined surfaces.

Aluminas of various kinds have been investigated for many years [6] because of their widespread use as catalyst, catalyst-support, and adsorbent materials. The role of surface hydroxyl groups on these materials has been repeatedly underscored for most, if not all, of the crystalline modifications of Al_2O_3 [7-12]. Much of the research on the catalytic properties of alumina has involved the γ modification because it can be prepared as a very high surface area material which, upon partial dehydration to expose Al^{3+} and O^{2-} ions, has excellent catalytic activity for alcohol dehydration [9-12], butene isomerization [13], catalytic cracking [14], and other reactions. The α-modification (corundum) is generally a lower surface area material which has lower catalytic activity. Nevertheless, the α-modification will chemisorb water in relatively large amounts and shows adsorption-desorption

characteristics very similar to the γ-modification [7,15,16]. Furthermore, it is available in single crystal form, and the (0001) crystal face has been studied using LEED [17-19] which shows the 1x1 pattern expected for a close packed layer of O^{2-} ions. Such a substrate has a very low surface area, compared to the powders normally used in adsorption and catalysis studies, but it is amenable to analysis by UPS as illustrated in this paper. Thus the single crystal α-alumina- water system can serve as a useful well-characterized reference system for which we can hope to gain a fairly detailed understanding of the surface composition and electronic structure.

II. Experimental

A standard ultra high vacuum apparatus, equipped with a differentially-pumped helium discharge source, an electron gun, and a cyclindrical mirror electron energy analyzer, was used for these experiments. UPS data were taken with the analyzer operating in the pulse counting mode. The scan time required for accumulation of reasonable spectra was three hours. Auger spectra were taken in the usual differential mode.

The substrate was a single crystal sample of α-alumina cut to expose the (0001) surface [17]. This substrate was mounted on a backing plate in which was imbedded a resistance heater constructed of 0.5 mm diameter platimum wire. The approximate temperature of the front face of the substrate was monitored with an iron-constantan thermocouple clamped to one corner of the front face. The sample, mounted on a standard sample manipulator, was placed so that the Auger and UPS probe beams approached the surface at grazing angles of 17^{o} and were coincident with the focal point of the analyzer, the axis of which was normal to the surface. Highly purified water was introduced through a variable leak valve.

III. Theoretical

The SCF-Xα-SW calculations were carried out in the muffin-tin approximation, employing tangent spheres whose radii were chosen to be proportional to the standard atomic or (for alumina) ionic radii, as closely as possible within the constraints imposed by the molecular geometry. The α-values computed by Schwartz [20] were used inside each atomic sphere, and an average of these values was employed for the intersphere and outer sphere regions.

Following Brower [21], the α-alumina lattice was represented by means of a single Al_2O_3 cluster in D_3 symmetry, based on the experimental geometry [22]. The $Al_2O_2(OH)_2$ model system was formed by adding H_2O across one of the Al-O bonds in the Al_2O_3 unit, with the Al-O (hydroxyl) bond length arbitrarily fixed at 1.369 Å. The resulting geometry is shown in Fig. 1. A minimal basis set of spherical harmonics was employed for this system. Furthermore, since our calculations for Al_2O_3 and for CH_3O-Al_2O_2-OH [23] show that the transition state energies are shifted uniformly from the ground state energies within the accuracy of our experimental data, we have calculated only one transition state for the $Al_2O_2(OH)_2$ system. The energies given in Table I for this system are therefore uniformly shifted ground state energies. A transition state was also calculated for the first electronic excitation (a'' → a'*), to give a band gap of 0.056 Ry (0.76 eV).

IV. Results and Discussion

An initial Auger spectrum of the α-alumina crystal surface revealed a large carbon-containing surface contaminant, which was removed by exposure to 5 X 10^{-5} torr of O_2 at approximately 550°C for a total of 14 hr. The surface remained essentially free of carbon contamination throughout the remainder of the experiment, as determined by Auger analysis. The UPS spectrum of this reference surface is shown in Fig. 2(a). Following 75 min. of exposure to 5 X 10^{-5} torr of water vapor at room temperature, the system was again evacuated to 1 X 10^{-8} torr and another UPS spectrum taken. The difference between this spectrum and the reference is shown in Fig. 2(b). Prior to taking the difference, the spectra were scaled to the same value at 11 eV kinetic energy. This point was chosen because it gave noise centered at zero counts in the high energy tail of the difference spectrum shown in Fig. 2b.

The Fermi level for these experimental spectra was determined, in a separate experiment, as the Fermi level of a metallic gold spot vapor-deposited on the α-alumina surface. In order to verify that the Fermi level was not shifted from one observation to another as the result of surface charging, the contact potential (which is the difference in work functions of the analyzer and the sample) was measured in each case by noting the onset of secondary electron emission. This onset was measured both under the usual UPS data gathering conditions described above and also with electron beam excitation at very low current (10^{-10} amp) in the pulse counting mode. Both measurements gave the same value,

2.1±0.10eV, for all conditions of the sapphire surface reported here. Evans [24] has shown that the low kinetic energy onset of secondary electron emission is equal to the contact potential. From a separate measurement of the work function of our spectrometer, using a grounded, clean Pd target, we have obtained the value 4.4 ± 0.1 eV. This leads to a value of 2.3 eV for the work function of aluminum oxide, which is in fair agreement with the value of 2.7 eV as determined by thermionic emission [25]. We conclude that net surface charging is absent, or at least quite small, in our experiments, and that it does not change significantly from one spectrum to another.

In order to interpret the features of the spectra of Fig. 2, we have compared the SCF-Xα-SW calculations described above with the experimental data. This was accomplished by aligning the $Al_2O_2(OH)_2$ energy level diagram in such a way that the center of the band gap coincides with the experimental Fermi level. Since the calculated band gap for Al_2O_3 [23] is smaller by a factor of 2.15 than the experimental value [26], the calculated gap for $Al_2O_2(OH)_2$ was first multiplied by this factor. Although there is no principled reason for believing that the calculated band gap for these two species are in error by the same multiplicative factor, we note that the calculated band gap for the $Al_2O_2(OH)_2$ species is quite small; even an error as large as the multiplicative factor we have used would not significantly affect the assignment of spectral features to which it leads. The resulting $Al_2O_2(OH)_2$

spectrum is given in Fig. 2(c). All of the energy levels arising from molecular orbitals composed primarily of 2p electrons on the various oxygen species are shown. The hydroxyl 2s levels, which fall far outside the range of the HeI radiation employed, have been omitted.

The experimental spectrum and the theoretical spectrum are in reasonable agreement. The large experimental peak at 4-8 eV kinetic energy is assigned to the hydroxyl species. Our model calculation represents hydroxyl sites with hydroxyl rather than oxide nearest neighbors [8,19,27]; thus we expect our model to correspond more nearly to a fully hydroxylated surface than to a highly dehydrated surface. Because the net negative charge on the hydroxyl oxygen will likely be larger when the hydroxyl is surrounded by oxide ions rather than by hydroxyl groups, we expect the electron binding energy to decrease as the number of oxide nearest neighbors increases. The surface corresponding to the spectrum of Fig. 2(a) was first dehydrated in vacuum at 550°C and retains a substantial concentration of surface hydroxyl species. Assuming that the dehydration process first removes chemisorbed molecular water and then, in spatially random fashion, weakly bound surface hydroxyl, we anticipate that dehydration at temperatures higher than 550°C should lead to an experimental spectrum in which the 4-8 volt peak is shifted slightly to the left in Fig. 2(a). Unfortunately, in the experimental configuration we used, the sample could not be heated above 550°C. The retention of a significant hydroxyl concentration on this single crystal

α-alumina substrate is very similar to the observations that have been made on powdered samples of α- and γ-alumina [8,15,27]. The experimental band from 11 to 18 eV is comprised of at least two bands. We suggest that these arise from two types of oxide species. Some support for this idea comes from a comparison of the $Al_2O_2(OH)_2$ calculations with our Al_2O_3 calculations [23]. Using the multiplicative factor of 2.15 discussed above and aligning the centers of the band gaps of the two calculations (i.e. forcing a common Fermi level), produces a composite spectrum with a large density of states in the 12-15 eV kinetic energy region due to oxide ions in the unperturbed oxide (Al_2O_3) and another group of states in the 15-18 eV kinetic energy region due to oxide ions perturbed by adjacent hydroxyls [$Al_2O_2(OH)_2$]. Substantiation of this proposal would require making UPS measurements at much lower hydroxyl coverages than reported here. The shift of the oxide 2p levels to lower binding energy upon adjacent hydroxyl adsorption is further confirmed by the fact that the theoretical muffin-tin sphere for the oxide ion encloses 4.2% more negative charge in the $Al_2O_2(OH)_2$ calculation than in the Al_2O_3 calculation, the oxide radii having been given the same value in the two cases.

The adsorption of water at 298K yields the difference spectrum shown in Fig. 2(b). Relative increases of the spectral intensity are noted on the low binding energy side of the hydroxyl oxygen region (~8 eV) and in the low binding energy part of the oxide region (15-17 eV) compared to Fig. 2(a). The most satisfying interpretation of these features, and one consistent with known properties of powdered α- and γ-alumina, involves molecular water

adsorption [8,15,16,27]. One way in which molecular water can be adsorbed which would give rise to the above features involves the interaction of the oxygen of the chemisorbing molecule with a Lewis acid site and of one of the hydrogens with a neighboring oxide. In this model the electron charge density at the oxide site would be significantly reduced. If this interpretation is correct, the spectrum requires that a sizeable reduction in charge density occurs--almost to the point of forming a full-fledged hydroxyl. This is not inconsistent with the observation by infrared and gravimetric measurements on powders that part of the molecularly adsorbed water forms surface hydroxyl as the substrate is heated [8]. Our own preliminary results of such heating experiments are inconclusive, but do suggest that significant hydroxyl structural changes do occur on heating. The adsorption of molecular water could also account for the relative enhancement in the oxide region (15 - 17 eV) since adsorbed molecular water will act to change the neighboring oxide environment in much the same way as a hydroxyl group.

There are other possible mechanisms which must be considered in discussing the above shifts. Infrared studies suggest that hydrogen bonding is extensive in regions of high hydroxyl coverage. We must then consider whether or not an increased hydrogen bonding upon water adsorption could give rise to the observed shift. In this case hydroxyl will act as both a proton donor and a proton acceptor so the net change in electron density on the hydroxyl oxygen is probably small. Local charge density variations might

also be a possible source. Peri's model [27] for hydroxyl behavior on γ-alumina predicts five different types of isolated hydroxyl sites.on severely dehydrated alumina, each having a different number of oxide near neighbors. The local charge density at these sites ranges from a deficiency of one electron to an excess of one electron. The more negative sites would be expected to have lower ionization potentials. However, it is difficult to rationalize the data of Fig. 3(b) in terms of this model. In the first place, our initial surface is sufficiently hydrated (>33%) that isolated hydroxyl groups are not expected to be the predominant species. Furthermore, sites of net positive and negative charge are removed at roughly the same rate during dehydration [27], so that the average ionization potential would not be expected to change significantly due to local charge variations.

V. Conclusions and Summary

From the above discussion we find that surface hydroxyl and oxide spectra are readily detected on the (0001) surface of α-alumina using HeI radiation and, under our conditions of quite low intensity, there is neglible problem with surface charging. The general features of the spectra are readily predicted by the model calculations using the SCF-Xα-SW method and a small cluster derived from one Al_2O_3 unit and one H_2O molecule. There is a definite difference between the spectrum from a surface partially

dehydrated at 550°C and the spectrum observed after the resulting surface is exposed to water at 25°C. This difference is discussed in terms of molecularly adsorbed water, but this interpretation must be regarded as speculative, supported only by other experimental evidence for molecularly held water [27] and by its feasibility. The theoretical calculations are of no help since molecularly held water is not considered. While calculations could certainly be done to investigate such geometries, we believe they would not be definitive since the small shifts produced experimentally could almost certainly be reproduced with a carefully chosen model geometry.

It is apparent that further experiments are needed if a reasonably clear interpretation of spectral shifts is to become available. In particular, experiments using an alternative experimental arrangement for high temperature (1000-1200°C) dehydration of single crystal and powdered α-alumina are in progress.

VI. Acknowledgement

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References

1. P. Day, ed., Electronic States of Inorganic Compounds: New Experimental Techniques. NATO Advanced Study Institutes Series (D. Reidal Pub. Co., Dordrecht, 1975), Series C, Vol. 20.

2. H.P. Bonzel and T.E. Fisher, Surface Sci. 51 (1975) 213.

3. J.C. Slater, J. Chem. Phys. 43 (1965) 5228.
J.C. Slater and K.H. Johnson, Phys. Rev. B5 (1972) 844.
K.H. Johnson, Adv. Quantum Chem. 7 (1973) 143.

4. J.C. Slater, The Self-Consistent Field for Molecules and Solids. (McGraw-Hill, New York, 1974), Vol. 4.

5. K.H. Johnson and R.P. Messmer, J. Vac. Sci. Technol. 11 (1974) 236.
I.P. Batra and O. Robaux, J. Vac. Sci. Technol. 12 (1975) 242.

6. For a review of aluminas see: B.C. Lippens and J.J. Steggerda, in "Physical and Chemical Aspects of Adsorbents and Catalysts", B.G. Linsen, Editor, (Academic Press, London, 1970) pp. 171-211.

7. R.L. Venable, W.H. Wade, and N. Hackerman, J. Phys. Chem. 69, 317 (1965).

8. J.B. Peri, J. Phys. Chem. 69, 211 (1965).

9. W. Hertl and A.M. Cuenca, J. Phys. Chem. 77, 1120 (1973).

10. T. Matsushima and J.M. White, J. Catal. (in press).

11. R.G. Greenler, J. Chem. Phys. 37, 2094 (1963).

12. M.P. Rosynek and F.L. Strey, J. Catal. 41, 312 (1976).

13. J.W. Hightower and W.K. Hall, J. Phys. Chem. 71, 1014 (1967).

14. W. K. Hall, F. E. Lutinski, and R. H. Gerberich, J. Catal. 3, 512 (1964).

15. R. L. Every, W. H. Wade, and N. Hackerman, J. Phys. Chem. 65, 937 (1961).

16. W. H. Wade and N. Hackerman, J. Phys, Chem. 64, 1196 (1960).

17. T.M. French and G.A. Somorjai, J. Phys. Chem. 74, 2489 (1970).

18. C.C. Chang, J. Appl. Phys. 39, 5570 (1968).

References (continued)

19. J.M. Charig, Appl. Phys. Lett. 10, 139 (1967).

20. K. Schwartz, Phys. Rev. B5, (1972) 2466.

21. K.L. Brower, J. Vac. Sci. Technol. 12 (1975) 458.

22. R.E. Newnham and Y.M. DeHaan, Z. Kristallogr. 117, (1962).

23. D.C. Foyt and J.M. White, J. Vac. Sci. Technol. 13, 334 (1976).

24. S. Evans, Chem. Phys. Letters 23, 134 (1973).

25. L.J. Rueger, F.C. Todd and H.R. Nelson, Battelle Memorial Institute Report S-725-4 to Aluminum Company of America, Aug., 1948; ALCOA Technical Paper No. 10, "Alumina Properties," 1960.

26. E.T. Arakawa and M.W. Williams, J. Phys. Chem. Solids 29 (1968) 735.

27. J.B. Peri, J. Phys. Chem. 69, 220 (1965).

TABLE I. SCF-Xα-SW Valence
Electron Energy Levels for $Al_2O_2(OH)_2$

Binding Energy (eV)	Symmetry	Origin
.817	a"	2p(O^-)
1.677	a"	2p(O^-)
2.077	a"	2p(O^-)
2.927	a'	2p(O^-)
3.687	a'	2p(O^-)
3.807	a'	2p(O^-)
10.14	a'	2p(OH)
10.38	a"	2p(OH)
10.93	a'	2p(OH)
11.16	a"	2p(OH)
12.06	a'	2p(OH)
13.33	a'	2p(OH)
15.40	a"	2s(O^-)
16.06	a'	2s(O^-)
26.19	a'	2s(OH)
27.18	a'	2s(OH)

Figure Captions

Figure 1. Geometry of the model $Al_2O_2(OH)_2$ unit.

Figure 2. Experimental and theoretical UPS spectra of a partially hydrated α-Al_2O_3 surface. The lower abscissa gives the measured electron kinetic energy while the upper scale give the electron binding energy with respect to the experimental Fermi level of the substrate. The four spectra represent the following: (a) reference surface prepared by heating 14 hr. in 5×10^{-5} torr of O_2 at 550°C; (b) change from reference after 75 min. exposure to 5×10^{-5} torr of water vapor at room temperature; (c) shifted SCF-Xα-SW spectrum for $Al_2O_2(OH)_2$.

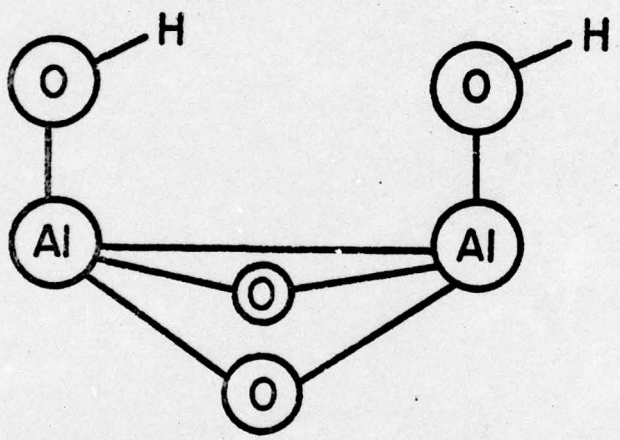
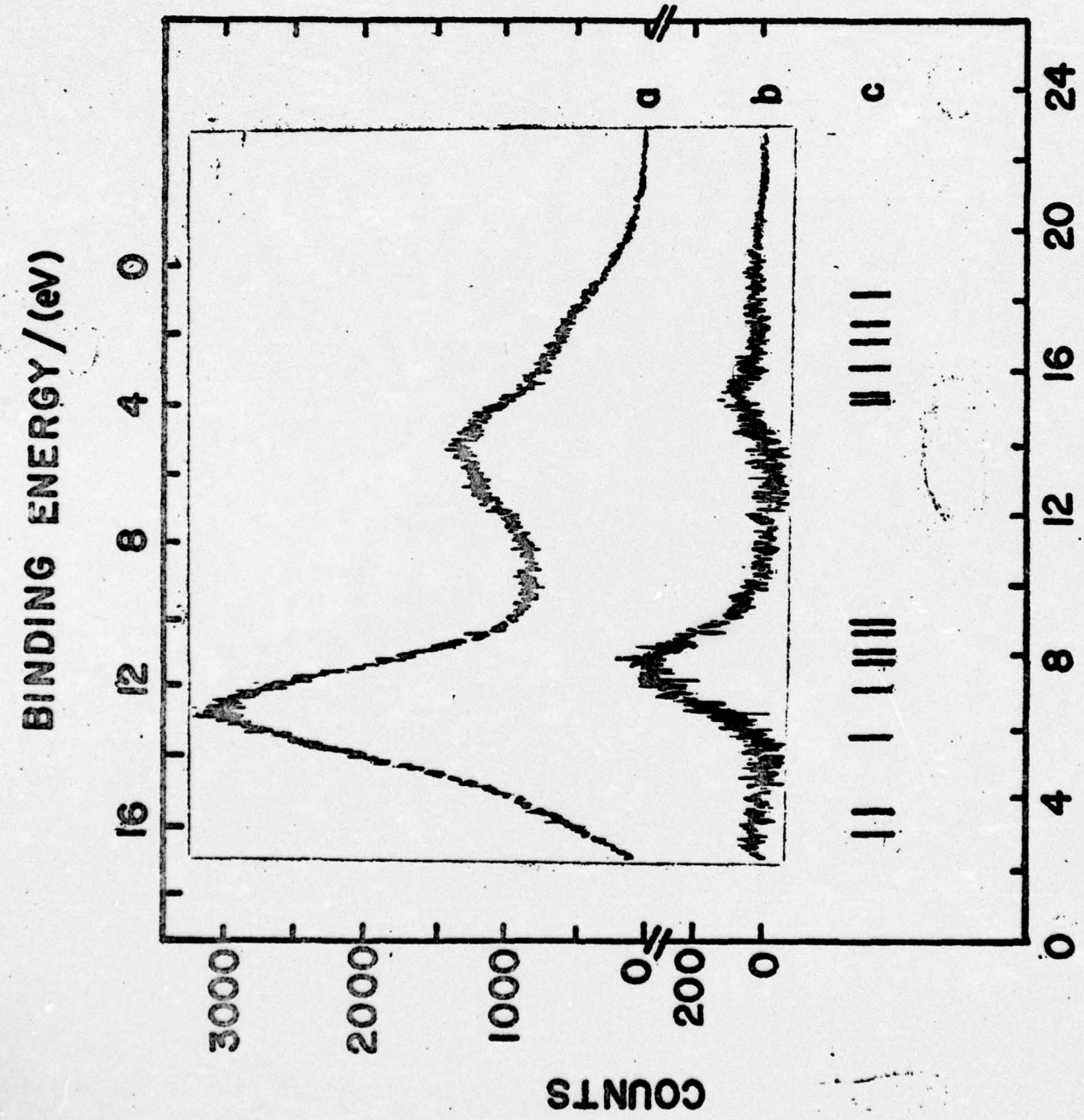


Figure 1

Figure 2


BINDING ENERGY/(eV)
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8
4
0
KINETIC ENERGY/(eV)
0
4
8
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COUNTS
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2000
1000
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200
0
a
b
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