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Interaction of ytterbium with solid ammonia and xenon studied using photoelectron spectroscopy

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Photoemission is used to examine valence electronic structure of Yb deposited on condensed ammonia or xenon films. The deposition of Yb onto solid ammonia produces a Yb phase whose two $4f$ peaks lie at a higher binding energy than Yb metal and also produces a feature near the Fermi level. The peak near E_f is not seen when Yb is isolated in xenon. From the appearance of the Yb $4f$ levels and the existence of a peak near E_f, it is concluded that the Yb is divalent and that (1) the peak near E_f is a shakedown satellite derived from the $4f$ states or (2) the peak near E_f is due to the hybridization of the Yb $4f$ states with other Yb or ligand states.

INTRODUCTION

One of the most interesting problems in physical chemistry is that of the solvation of metals in liquid ammonia.[1-12] At low temperatures, ammonia solidifies and the low vapor pressure solid can be used in a vacuum environment to study the interaction between metals and ammonia. We have used this technique to conduct photoemission experiments designed to study the solvation of alkali metals in ammonia. Photoelectron spectroscopy is an excellent technique for studying changes in the electronic structure and the formation of chemical species. Earlier studies of the solvation of alkali metals in ammonia at 80 K showed that Na and K solvated in ammonia but also showed that Cs formed a metal-amine at 80 K.[13] In the solid state, the mixing of the metal with ammonia is limited and the metal concentration at the surface quickly exceeds that which can be solvated. When this happens, the metal atoms cluster and form a metallic phase. Metal/solid ammonia films have a very small work function and are sensitive to light and heat.[14] Photoemission studies of metal/solid ammonia systems are also complicated by the fact that the films are heterogeneous and thermal- or photon-driven chemical or physical processes with a relatively long-time scale continue at 80 K.

This paper describes some photoemission studies of Yb-solid ammonia films formed by the deposition of Yb into a thin solid ammonia film. Like our previous work with the alkali metals, the valence-band data for the systems will be examined to identify the physical or chemical process taking place in the Yb-NH_3 films. Unlike the alkali metals, the rare earths have relatively narrow $4f$ bands at or near the Fermi surface. These $4f$ states are responsible for many interesting physical phenomena in other rare-earth compounds and are a sensitive indicator of the electronic configuration of a rare-earth-like Yb.[15-18] The paper also reports results for Yb isolated on a solid xenon film. The work with the Yb clusters in xenon shows the expected evolution of the electronic structure of Yb as a function of cluster size and provides a reference for identifying the differences when Yb interacts with NH_3.

EXPERIMENTAL PROCEDURE

The experiments were performed using a cold finger which was installed in a stainless steel ultrahigh vacuum system equipped for surface analysis. The cold finger was cooled to ~80 K using liquid nitrogen or ~20 K using liquid helium. Our sample support was a recrystallized Ta(110) strip that could be resistively heated to incandescence while the cryostat was cold to clean the tantalum surface. After the Ta foil had been sufficiently degassed and surface contamination removed by resistive heating, Xe or NH_3 films were deposited on the Ta support. During some of the experiments, it was necessary to suppress the strong photoemission from the Ta $5d$ states. In those experiments the Ta strip was coated with a thick aluminum film before the Xe or NH_3 was deposited. The Yb films were grown using a resistively heated source (Yb chunks in a tungsten basket). The amount of Yb deposited in a given evaporation at constant power was determined by recording the deposition time in seconds and converting time to the number of Yb atoms deposited using a scaling factor. The scaling factor was deduced by growing Yb films on the Ta substrate and measuring the attenuation of the Ta $4f$ states to get the film thickness in monolayers. A value of 4.3×10^{15} Yb atoms per cm^2 was used to convert from the film thickness in monolayers to the number of Yb atoms deposited per second.

The photoemission work was done using the He I (21.2 eV) emission from a water-cooled He plasma source. A double-pass cylindrical mirror analyzer operated in the retarding mode detected and energy analyzed the photoelectrons. The Ta support was oriented in the usual manner with the photon beam incident on the sample at 45° and the Ta foil's normal vector along the cylindrical mirror analyzer acceptance cone.

EXPERIMENTAL RESULTS

Figure 1 shows data for Yb isolated in condensed NH_3 at liquid-nitrogen temperature (~80 K). For an Yb coverage estimated to be 7.6×10^{13} Yb atoms/cm^2, the Yb $4f$ peaks (labeled a_1 and a_2) are found near -2.1 and -3.4 eV, respectively. The peaks grow with Yb coverage and

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are the strongest Yb features when the Yb coverage has been increased by a factor of six to 4.6×10^{14} Yb atoms/cm^2. The Yb 4f spectra for Yb/NH_3 do not look like the spectra for metallic Yb shown at the top of Fig. 1. This suggests that (1) Yb dissolves into the NH_3 and possibly that (2) Yb has a chemical interaction with the ammonia. An additional peak marked "x" is seen near the Fermi level and is comparable in intensity to the Yb 4f levels for the greatest Yb deposition studied.

The binding energy and intensity of the Yb 4f states for Yb/NH_3 can be contrasted with the behavior of the Yb 4f states for comparable amounts of Yb deposited on a xenon film. Figure 2 shows the results for depositing small amounts ($\theta<0.5$ ML) of Yb on a solid xenon film at 20 K. The electronic structure of the Yb evolves rapidly with Yb coverage and by the time enough Yb ($\theta=1.6\times10^{14}$ atoms/cm^2) has been deposited to clearly see the Yb 4f states, the spectra are already show both the bulklike and surfacelike 4f components. This implies that the agglomeration of the Yb has advanced to the point that the Yb clusters are big enough to have both surface and bulk atom sites. The Yb 4f peaks for the clusters lie near the binding energies of the 4f states observed for the metallic Yb film, but the peaks for the clusters are broader and show somewhat different intensities. Clearly there is a lot going on in these spectra and this is not unexpected, since, we believe that a distribution of clusters with different sizes has been produced. The important result illustrated in Fig. 2 is that relatively small amounts of Yb agglomerate to form clusters which are large enough to have an electronic structure resembling metallic Yb. This happens because the interaction driving the mixing of Yb with the matrix is absent in Xe.

Another facet of the data shown in Fig. 2 is the position of the Yb S_1 and S_2 components for the clusters when compared to metallic Yb. Surface components for the clusters are shifted about 0.3 eV to higher binding energy when compared to the S_1 and S_2 components for the film. Schneider, Laubschat, and Reihl[17] have seen similar changes in the 4f spectra for Yb films deposited on cold surfaces where roughening was expected. Rougher films have an increased number of low coordination surface sites and Schneider, Laubschat, and Reihl[17] made a connection between the surface coordination and the binding energy of the 4f states. Using the work of Schneider, Laubschat, and Reihl,[17] we conclude that the majority of surface Yb atoms for the Xe matrix-isolated clusters have a coordination number of 7, while those for

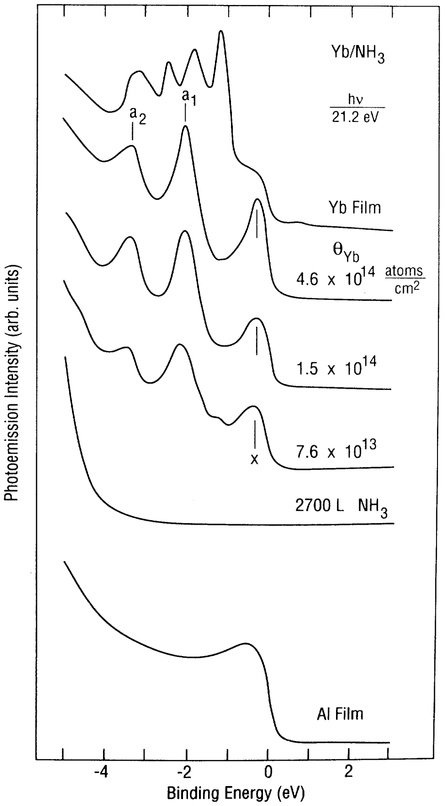

FIG. 1. Energy-distribution curves (EDC's) for Yb deposited onto solid NH_3 at liquid-nitrogen temperature. The deposition of Yb onto solid ammonia produces the divalent species with Yb 4f peaks marked "a_1" and "a_2." The peak marked "x" grows with increasing Yb coverage.

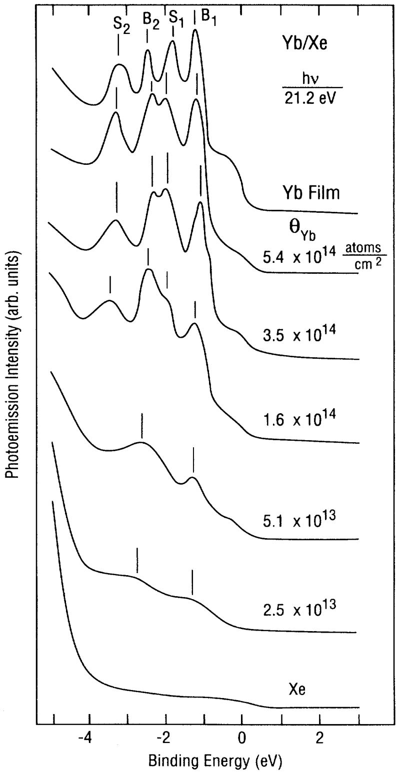

FIG. 2. Photoelectron spectra for Yb isolated in solid xenon. This experiment was performed to study the modification of the 4f features due to clustering. The vertical lines mark the position of various Yb 4f components including the bulk ($B1$ and $B2$) and surface ($S1$ and $S2$) peaks.

an Yb film on Ta(110) have the expected coordination of the fcc (111) surface (i.e., 9).

In experiments with alkali metals,[19] it was found that the physical and chemical behavior of alkali metals in ammonia at liquid-nitrogen temperatures is different than that at liquid-helium temperatures. In order to change the physical conditions during Yb deposition and determine whether the mixing of Yb with NH_3 and the subsequent valence changes are temperature dependent, the Yb/NH_3 experiment was repeated at liquid-helium temperatures (~ 20 K) and the results are shown in Fig. 3. When small amounts of Yb (i.e., 2.5×10^{13} atoms/cm^2) are deposited on NH_3, at 20 K (Fig. 3 bottom curve), the spectrum was similar to that seen when Yb is deposited on NH_3 at 80 K. The Yb $4f$ peaks marked a_1 and a_2 are at the same binding energies and the state marked "x" near the Fermi level is as intense as the Yb $4f$ features. It is obvious that Yb and NH_3 react at the surface to form the same Yb-NH_3 species at 20 as at 80 K. We think this happens because the incident Yb atoms come from a hot evaporation source. The Yb atoms have to thermalize when implanted in the NH_3 matrix and have sufficient energy to react with the NH_3. Very different results might be obtained with cold beam of Yb atoms. The low temperature has a clear affect on the extent of the mixing between the Yb and NH_3. When the number of Yb atoms is effectively doubled, peaks a_1 and a_2 appear, and we interpret this as indicating that small Yb clusters begin to form. The Yb in these clusters is bonded to NH_3. At this point the Yb-NH_3 film is a mixture of two phases because the a_1 and a_2 components identified with the Yb-NH_3 compound or the solvated Yb^{2+} (divalent) are seen. Adding more Yb produces the bulk Yb $4f$ components (marked b_1 and b_2) characteristic of metallic Yb. After depositing 2.2×10^{14} Yb atoms/cm^2, the depositions were halted and the film was warmed from 20 K to 40–50 K and 80 K, respectively.

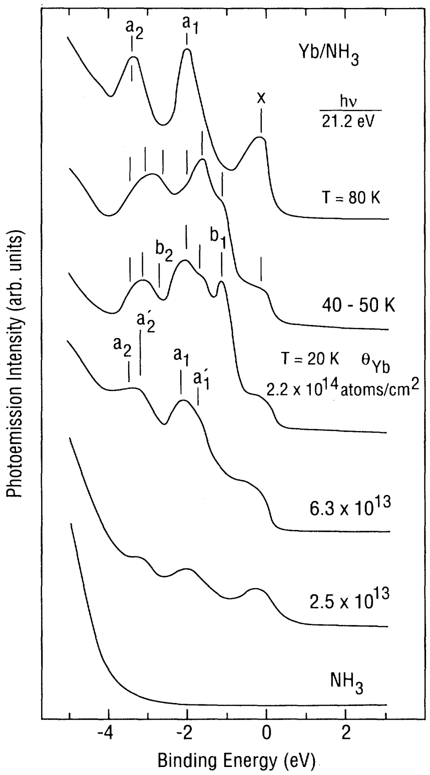

FIG. 3. Photoelectron EDC's for Yb deposited onto solid NH_3 at liquid-helium temperatures. This figure shows the influence of temperature on the NH_3-Yb interaction. When Yb is initially deposited on ammonia at 20 K, peaks (a_1 and a_2) related to a divalent species form. At later stages of Yb deposition, peaks (a'_1 and a'_2) related to Yb clustering and (b_1 and b_2) related to metallic Yb are seen. Annealing the Yb containing NH_3 film, converts the cluster related and metallic components into the divalent species giving rise to a_1 and a_2.

At 40–50 K, there is spectral evidence that the larger Yb particles begin to dissolve into the NH_3 and become smaller. The bulk Yb $4f$ peaks (b_1 and b_2) decrease in intensity and the a'_1 and a'_2 peaks become larger. We feel this shows that the larger Yb clusters breakup into smaller clusters. The a_1 and a_2 peaks also become smaller. The reduction in the intensity of the a_1 and a_2 peaks could be due to the incorporation of the isolated Yb atoms into the Yb clusters. When the temperature was raised to 80 K, the metallic Yb components (b_1 and b_2) and the cluster-related (a'_1 and a'_2) Yb components disappear and all of the Yb is in the divalent Yb phase (a_1 and a_2 peaks) characteristic of dilute amounts of Yb in NH_3. This is interpreted as the complete dissolution of all of the Yb clusters into the NH_3 matrix. Thus, the activation temperature for mixing the Yb and NH_3 is above ~ 40 K but below ~ 80 K.

DISCUSSION

Photoemission has been used to study the electronic structure of vapor phase Yb,[20] Yb metal surfaces,[17,21] Yb films on other metal surfaces,[22,23] and a number of Yb intermetallic compounds.[24] Yb has received such thorough study because the closed-shell structure of the Yb $4f$ levels provides an opportunity to study photoionization dynamics and because holes in the Yb $4f$ states behave like the $4f$ electrons in cerium.[23] Much of the attention paid to Yb compounds is also derived from an interest in heavy-fermion systems.[25–28]

Work by others on Yb (Refs. 15–18) shows that the occupation of the Yb $4f$ states controls the appearance of the $4f$ levels. The multiplet structure of Yb is governed by the occupation of the $4f$ states and is a $4f^{14}$ (closed-shell) initial state for atomic and divalent Yb (Yb^0 and Yb^{2+}, respectively) and a $4f^{13}$ initial state for trivalent Yb (Yb^{3+}). In the case of zero and divalent Yb, filling of the $4f$ shell is achieved by promoting or hybridizing a $5d$ electron. The $4f$ multiplets for Yb^0 and Yb^{2+} which have a $4f^{13}$ final state are spin-orbit split into a doublet that has a spin-orbit splitting of ~ 1.3 eV.[17,20] In the metallic phase, there are two $4f$ doublets which have been interpreted as the bulk and surface components. For metallic Yb, the states nearest the Fermi edge have been attributed to the 5*d* band, which is just barely occupied and the 6*s* band. X-ray-absorption data and theory indicate that the *d*-bandwidth is ~ 8 eV.[24] For the atomic Yb, the least tightly bound level is the 6*s* state. This peak for Yb vapor is almost as intense as the 4*f* levels at 20-eV photon energy. When Yb interacts with another metal, either in an intermetallic compound or when deposited on another metal, it can have a mixed valence.[15–18] This has been attributed to changes in the on-site 4*f*-*d* hybridization and hybridization with other nearest-neighbor electronic states that put holes in the 4*f* shell. When the trivalent Yb is present, the valence 4*f* states seen in photoemission are far more complex. Trivalent Yb has a 4*f* multiplet spectrum that extends from -5- to -16-eV binding energy.

The data for Yb isolated in NH_3 shows that the interaction between NH_3 and Yb produces an Yb species with a closed 4*f* shell. For the Yb matrix isolated in NH_3, the Yb 4*f* peaks are at -2.1- and -3.4-eV binding energy, the measured spin-orbit splitting is 1.3 eV. The peaks at -2.1 and -3.4 eV are identified with a divalent Yb-NH_3 species based on their intensity and splitting, which matches the expected spin-orbit splitting for Yb^{2+}. This species might be $Yb(NH_3)_6$ given that this compound is formed when liquid Yb-NH_3 solutions are cooled or it could be the divalent amide $Yb(NH_2)_2$.[29]

A very interesting feature of the valence-band spectrum for Yb dispersed in solid NH_3 is the peak seen near the Fermi level. At the present time, it is not clear what this peak signifies. A similar feature is seen in some Yb intermetallic compounds (i.e., $YbAl_2$ or $YbCu_2$) and was attributed to 4*f* states. These compounds are mixed valent and show Kondo behavior. If the peak is taken to be the Yb $4f_{7/2}$ feature, a second peak ($4f_{5/2}$) component should be located ~ -1.3 eV from the $4f_{7/2}$ feature. An examination of our spectra [Fig. 1 (5th curve) or Fig. 3 (top curve)], shows that such a peak would overlap with the feature a_1. Unfortunately, our data is not resolved well enough to demonstrate that the $4f_{5/2}$ peak exists but an examination of the heights of peaks a_1' and a_2' suggests that the branching ratio is smaller than that expected for the 4*f* doublet. This could be interpreted as showing that peak a_1 consists of two unresolved components (the $4f_{7/2}$ component paired with the peak a_2 and $4f_{5/2}$ component paired with the $4f_{7/2}$ component marked "*x*").

If the assignment of states as just discussed is made, the electronic structure of Yb species seen in the Yb-NH_3 mixture may have similarities to the mixed valent intermetallics studied by those interested in the Kondo problem and heavy fermions. The movement of 4*f* states to the Fermi energy implies a hybridization of 4*f* states with either ligand states or on site Yb *d* states that would make the Yb mixed valent. The existence of a mixed divalent/trivalent state for the Yb/NH_3 is supported by bulk magnetic studies of $Yb(NH_3)_6$. $Yb(NH_3)_6$ is weakly magnetic at low temperatures ($\sim 0.52\mu_b$/atom) and this would not be expected for a purely divalent Yb species which has a closed *f* shell.[29] It is unjustified to read more into the data given by this experiment and recent studies of the temperature dependence of the $4f_{7/2}$ peak in other Yb compounds taken to be the Kondo resonance in compounds like $YbAl_3$ has cast doubt on such interpretation.

Another possibility is that the feature is due to the localization of the 6*s* electron on the Yb (i.e., Yb isolated in its atomic state) or the hybridization of the 6*s* state with the NH_3 levels. The NH_3 molecule is characterized by a simple electronic structure. Three states of the ammonia are filled and the highest filled level the $3a_1$ is about 10 eV below the vacuum level. In the solid or liquid, the NH_3 molecular levels would be expected to interact and broaden into a filled valence band. Thus, solid ammonia can be thought of as a wide gap semiconductor or insulator with a band gap of about 5 eV.[4,7] In such a material the binding of the electron in solid ammonia would be treated like the donation of charge from a semiconductor dopant. The ionization potentials of all of the metals known to solvate in NH_3 are ~ 5 eV. From the location of the solid NH_3 $3a_1$ level for the NH_3 film on a metal support, we see that the Fermi level is pinned near the unoccupied NH_3 state. If the Yb is ionized, the 6*s* electron would be donated to the unoccupied NH_3 band and a divalent or trivalent Yb ion formed.

Finally, the peak near the Fermi level could be due to a two-electron photoemission process. Two-electron photoemission processes are likely in highly correlated electronic systems such as the rare-earth compounds and the Yb 4*f* states in the case of Yb/NH_3 are highly correlated given the narrow 4*f* state bandwidth. The location of the Yb 5*d* band near the Fermi energy and possible bonding of Yb to an NH_3 or NH_2 ligand also helps to make the possibility of Coulomb effects very likely. A comparison of the data with that available for cerium and cerium compounds[23] suggests that the Yb 4*f* doublets (a_1 and a_2) for the Yb-NH_3 compound are the poorly screened (4*f* levels) and the peak (*x*) seen near the Fermi level is one of the well screened 4*f* levels. In other words, the peak in the spectrum near the Fermi level is due to a "shake down" process, which is a final-state effect. The positive charge pulls the Yb 5*d* states to the Fermi level, where electrons can be transferred from the ligands into the *d* band leading to a transfer of charge onto the Yb site. The relative amplitudes of two sets of 4*f* features are related to the probability of charge transfers to the Yb site in the time of the photoemission event. We argue that the peak near the Fermi level is not the 6*s* state as was seen for atomic Yb.[20] The most likely explanations for the valence electronic feature at the Fermi energy are (1) a two-electron "shakedown" process or (2) hybridization of the 4*f* states with *d* states or ligand states at the Fermi energy.

CONCLUSIONS

In this paper, we have presented data for Yb in several distinct environments. When Yb is deposited onto NH_3 at ~ 20 or ~ 80 K, the Yb atoms interact with the NH_3 and form a species that is divalent ($4f^{14}$ initial state). The mixing of Yb and NH_3 at 80 K is thermodynamically favored but is limited at 20 K. The mixing of Yb in NH_3 when heated from 20 K to near 80 K is demonstrated by the transformation of surface and bulk features of metallic Yb into two peaks, which we call a_1 and a_2 and a peak called "x," which appears near the Fermi level. The feature "x" near E_f could be due to the interaction between Yb and NH_3, or a breakdown in the one-electron photoemission process. Most probably, the feature near E_f is a "shakedown" peak. However, there is also the possibility of hybridization of the Yb $4f$ levels with the on-site d states or ligand states which can put $4f$ states at the Fermi level as is observed in heavy-fermion systems like $YbAl_3$ or $YbCu_2$.

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