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Photoemission studies of the metal-nonmetal transition of sodium on solid ammonia

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Photoemission experiments were performed to investigate the properties of Na on solid ammonia. At low coverages of Na on solid NH_3 a nonmetallic feature of the Na $2p$ core level is seen at 33 eV binding energy, which is 2.4 eV deeper than that of the metallic Na $2p$ core level. This higher-binding-energy features is thought to be due to solvated Na atoms in the NH_3 matrix. At higher coverages it appears that a metallic phase of the Na atoms occurs, along with the appearance of a plasmon loss feature. It was found that the metal-nonmetal transition is associated with these two Na core-level features, coexisting at intermediate Na coverages. This regime is consistent with a phase-separation regime where metallic clusters coexist with a dilute phase which has Na solvated in the NH_3. Another fascinating feature of this Na–solid-NH_3 system is a work-function value as low as 0.9 eV when Na and NH_3 are codeposited at 80 K.

The subject of alkali metals dissolved in liquid ammonia has been studied for more than a century and the metal-nonmetal transition in these systems[1] is of great interest because of a rich variety of physical behavior observed from sufficiently dilute metal-NH_3 solutions which are nonmetallic, to higher metal concentrations where metallic states occur. In the intermediate range of concentrations, there is a miscibility gap in the phase diagrams of many metal-NH_3 solutions[2–5] over a broad range of temperatures and compositions. By now there have been many experimental and theoretical investigations[6–9] on the thermodynamic and magnetic properties in metal-NH_3 solutions, and in addition various theories of the metal-nonmetal transition have been considered. For example, Cohen and Jortner made the hypothesis that the metal-nonmetal transition is intermediated by microscopic inhomogeneities in the metal-NH_3 solutions,[10] where as Mott has proposed that the solubility gap is a direct and necessary consequence of a metal-nonmetal transition of the "Mott-Hubbard type" in metal-NH_3 solutions.[11] In contrast to extensive work concerning alkalis in liquid ammonia, little is known about the interaction of alkalis with solid ammonia. In the work reported here, we carried out photoemission measurements of both Na deposited on solid NH_3 and solid NH_3 deposited on Na, to try to investigate the nature of the metal-nonmetal transition. We also compare these results to that of Na deposited on solid oxygen which is believed to be a system without any solvation, and also briefly mention the sodium tungsten bronzes which also show a metal-nonmetal transition.[12]

Core-level investigations were made using tunable monochromatized synchrotron radiation provided by the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Photoemission measurements were performed in a vacuum chamber operating with a base pressure of 2×10^{-10} Torr. Surface cleaning for the Ta substrate was accomplished, and could be regenerated, by resistive heating. Solid NH_3 layers were condensed at liquid-nitrogen temperature on a Ta substrate and varying amounts of Na were then evaporated from a getter source onto the NH_3 layers. Photoemission data were collected using a Vacuum Generators spherical analyzer and the total resolution at photon energy 75 eV was 0.6 eV. The attenuation of the various photoemission peaks was used to calibrate the Na overlayers, as well as to verify the absence of contamination during the course of measurements. The experimental procedures for solid NH_3 condensed on Na layers were similar to that described above. Values of the work function were estimated by the usual technique of measuring the low kinetic energy cutoff in the photoemission spectrum.

Figure 1 shows the energy distribution spectra for different Na coverages on solid NH_3. Spectrum (a) denotes the symmetric $2a_1$ orbital energy level of solid NH_3. At about 10 monolayers (ML) coverage of solid NH_3 on Ta, which was estimated from the reduction of the underlying substrate features, the Fermi level of the Ta substrate was almost unobservable. The initial small amount of Na, 1.2×10^{13} atoms/cm^2, gives a single peak at binding energy 33 eV, shown in spectrum (b), which is believed to be a Na $2p$ core level. As more Na was added there was a shift to shallower binding energies which can be seen from spectra (b)–(d). One striking feature seen in spectrum (e) is that a low-binding-energy peak, at 30.6 eV, appears at this higher coverage of 7.0×10^{14} atoms/cm^2, and an associated Na plasmon peak is observed at 36.6 eV. In spectra (f) and (g), the low-binding-energy peak enhances and shifts slightly to lower binding energy, and the plasmon feature becomes pronounced. At a coverage of 4.1×10^{15} Na atoms/cm^2, the high-binding-energy feature of Na is now small enough so that it becomes a shoulder of the lower-binding-energy peak, which is shown in the spectrum (g) in Fig. 1 and the first spectrum from the bottom in Fig. 2. We have examined these two different peak energies of 33 and 30.6 eV and

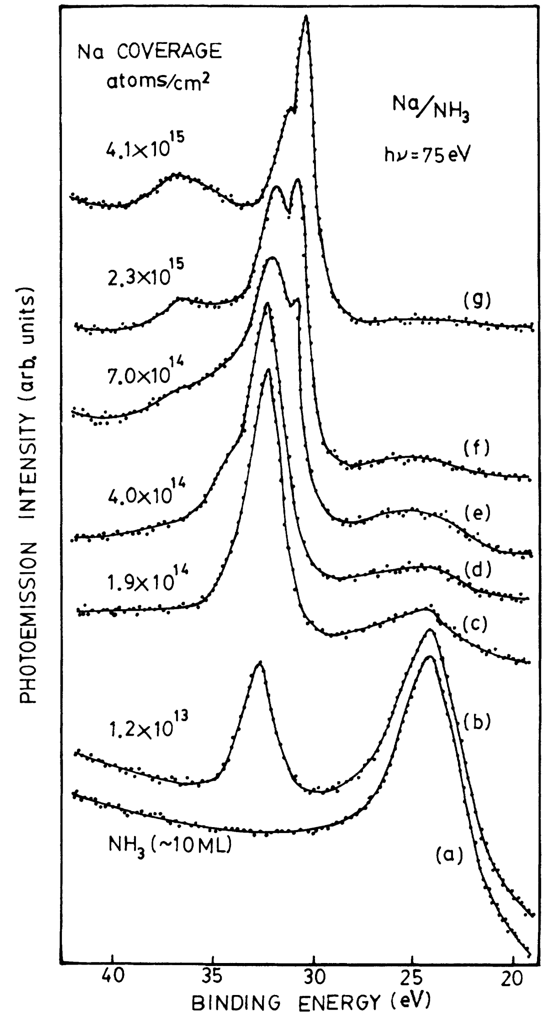

FIG. 1. Photoemission spectra of Na $2p$ core level for different Na coverages on solid NH_3 at photon energy 75 eV and temperature 80 K.

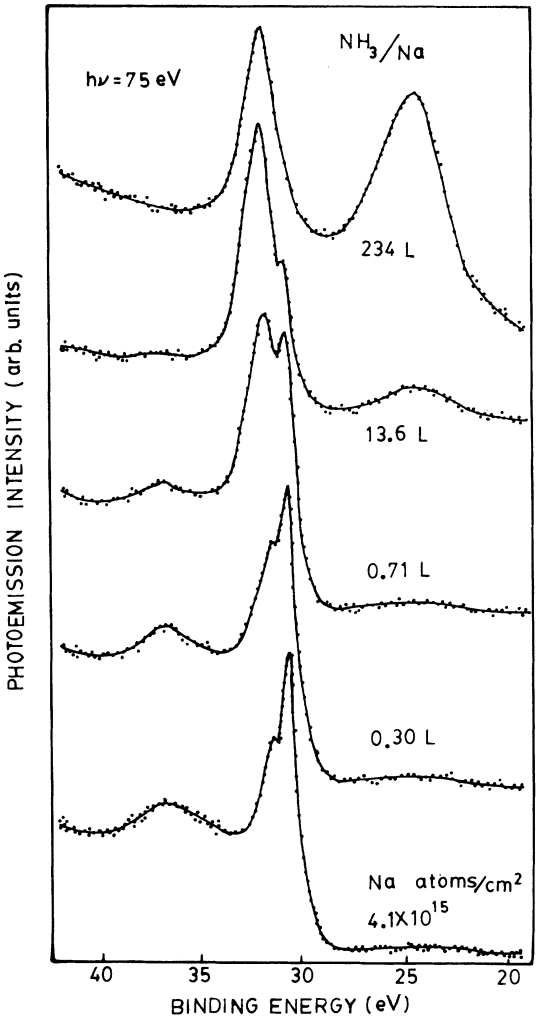

FIG. 2. The evolution of the double peak structure of the Na $2p$ core level as solid NH_3 put over a Na layer which was initially deposited on solid NH_3. The exposures are given in langmuirs $(L)=1\times10^{-6}$ Torr sec.

found that the peak on the right-hand side (at 30.6 eV) is the metallic Na $2p$ core level which has been previously observed at 30.58 eV using Al $K\alpha$ radiation.[13] The plasmon energy loss at 6 eV from the $2p$ level is in good agreement with that expected from free-electron calculations.[14] We emphasize that this double peak structure is not due to a surface-bulk shift of the Na $2p$ core level which is only about 0.3 eV.[15] If solid NH_3 is now put over this Na layer, we observe that the higher-binding-energy peak of the Na $2p$ level reappears and the intensity of the lower binding energy (i.e., metallic) feature decreases and finally disappears at greater exposures of NH_3 (shown in Fig. 2). We take this as evidence of Na dissolving in the new ammonia layer.

It is well established that, in extremely dilute solutions of alkali metals in liquid NH_3 which are nonmetallic, the metal is completely dissociated into metal ions and solvated electrons. In the case of Na in solid NH_3 this also appears to be true. In our experiments, the solubility of Na in solid NH_3 is confirmed not only by putting NH_3 over the Na layer as already described, but also by data (not shown here) which show the decrease of the metallic component and the associated plasmon feature, and the increase of the high-binding-energy component of the double peak structure as a function of time. This is interpreted as the continued slow dissolving of Na at the surface into the solid NH_3 layer at 80 K, and the high binding energy can be attributed to the ionic state of Na in the ammonia matrix. The binding energy of the Na $2p$ core level in an ionic state can also be seen in the alkali halides.[16] We mention that this feature at 33 eV cannot be assigned to the atomic state of Na which is much deeper, at 38 eV, with respect to the vacuum level.[17,18]

The intensity of the high-binding-energy feature of the solvated Na $2p$ core level in the nonmetallic state as a function of the coverage of Na, is plotted in Fig. 3(a). At low coverages of Na the peak increases in magnitude as more Na is deposited, while it decreases in intensity as

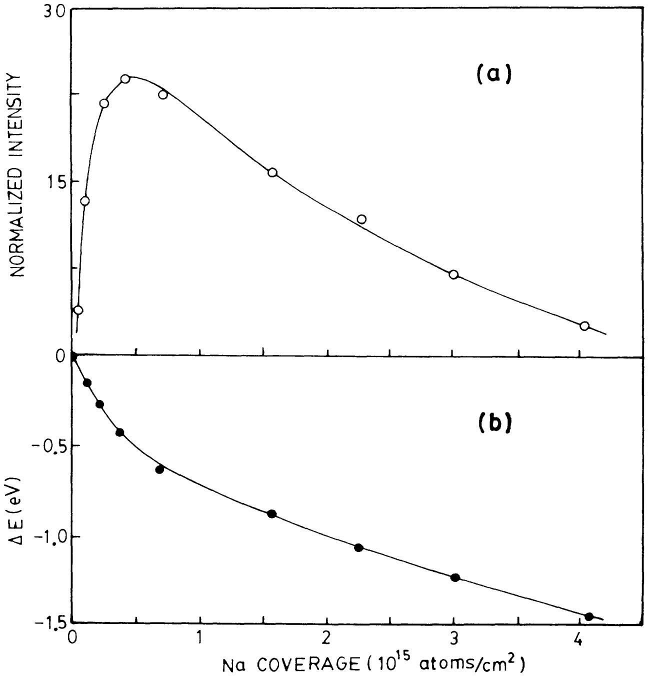

FIG. 3. (a) The normalized intensity of the high-binding-energy feature of the Na $2p$ core level as a function of the coverage of Na. (b) The shift of the high-binding-energy feature of the Na $2p$ core level relative to its initial position [Fig. 1(b)] as a function of the coverage of Na.

the metallic feature grows. The solvated Na feature also shifts toward lower binding energy as more Na is deposited. The shift of this feature relative to its initial position as a function of the coverage of Na is plotted in Fig. 3(b). The initial shift of the solvated Na peak is most rapid for low concentrations, and then there is a decreasing rate when the metallic phase appears. This can probably be understood as follows. Even though the low-frequency dielectric constant of ammonia is large, the high-frequency dielectric constant of ammonia is relatively small, and the addition of Na and the accompanying solvated electrons must increase the screening response and the dielectric constant at high frequency, near 10^{-15} sec, i.e., the time for a photoemission event. This enhanced screening causes a shift to lower binding energy with increasing electron density. In a two phase region, the metallic phase will also screen the Na atoms in the solvated phase, but probably not as effectively as the increased solvated electron density. This would explain the smaller shift of the high-binding-energy feature after the metal peak is evident.

In Fig. 1 it can be seen that at coverages up to 2×10^{14} atoms/cm^2 there is only evidence of one Na environment, which we identify as the dilute or solvated phase. If we argue that the Na dissolves in a few layers at the solid NH_3 surface then one can estimate that the solvated phase exists up to concentrations of about 3%. Above this value there is evidence for metallic Na, and the two peak structure of the Na $2p$ core level in Figs. 1(e), 1(f), and 1(g) is taken as evidence of coexistence between the dilute phase and a metallic phase (probably Na clusters). The phase diagram for Na in NH_3 has apparently not been studied down to 80 K, but extrapolations indicate probable Na concentrations much less than 1%.[19] In fact, other workers[20] have indicated no solubility of Na in NH_3 below $-110\,^\circ$C. Hence the observation of solvated species in these experiments may indicate a unique solubility of Na in NH_3 in a surface region at 80 K.

A different interpretation is based on the possibility that the species $Na(NH_3)_x$ may exist.[20] In the Li system, where $Li(NH_3)_4$ is thought to exist, the phase diagram at low temperatures shows a dilute regime[20] where solid $Li(NH_3)_4$ and solid NH_3 coexist, and a high-concentration regime where solid Li coexists with solid $Li(NH_3)_4$. The Na analogue of this would explain our observations, since the single peak regime would be due to coexistence of $Na(NH_3)_x$ and solid NH_3, and the two peak structure would be where $Na(NH_3)_x$ coexists with solid Na. The possibility that $Na(NH_3)_6$ does exist (i.e., $x=6$) has been discussed by Sienko.[20] We point out that

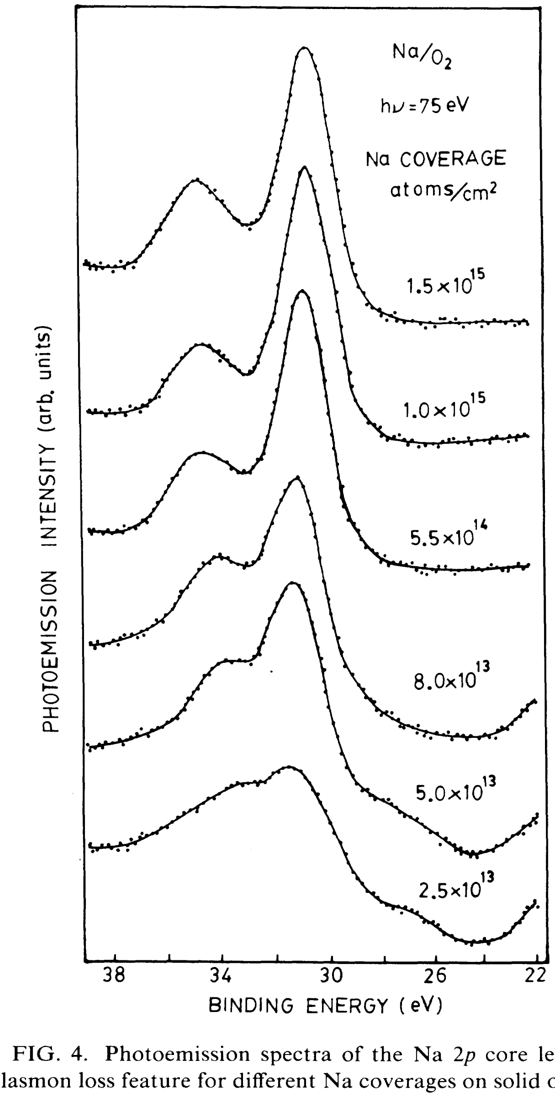

FIG. 4. Photoemission spectra of the Na $2p$ core level and plasmon loss feature for different Na coverages on solid oxygen.

in an interesting work by York and Solin[21] on K-ammonia-graphite intercalation compounds, various K-ammonia compounds have been identified.

Another system, Na_xWO_3, also shows a metal-nonmetal transition when the Na concentration approaches $x = 0.25$.[12] We briefly mention that in this case the Na $2p$ core-level photoemission spectra are very similar to the case of the $Na\text{-}NH_3$ system in which the higher-binding-energy peak appears at lower concentrations and a second peak is observed at lower binding energy with higher Na concentrations. Although the mechanism for the metal-nonmetal transition is undoubtedly different in the Na_xWO_3 and $Na\text{-}NH_3$ systems, the approximately 1-eV higher-binding-energy peak observed at lower Na concentrations of Na_xWO_3 should not be claimed to be due to a Na $2p$ surface sensitive component.

For comparison, with a different kind of behavior, the features of Na deposited on a layer of solid oxygen are shown in Fig. 4. It can be seen that the metallic Na $2p$ core level shifts gradually to lower binding energy with increasing amounts of Na, which is perhaps expected as one goes from Na in contact with oxygen to a more metallic environment. It is clear that there is no evidence of solvation or a mixed phase regime for Na on solid oxygen. It is interesting that even for relatively small amounts of Na, the plasmon loss feature exists. As more Na is deposited the electron density in the surface layer increases and hence, the plasmon pattern shifts monotonically toward its bulk value. The broader line width of the Na $2p$ core level shown in Fig. 4 is a characteristic of the oxidation of Na. It is probable that after the initial formation of a superoxide or peroxide, where either one or two Na electrons are donated to an O_2 molecule, the Na forms clusters and a metallic phase. This will be investigated in further studies.

Another interesting feature of the Na–solid-NH_3 system is its low work function. The work function of the clean Ta substrate was 4.4 eV. After a few layers of solid NH_3 were condensed on Ta, the work function was reduced to 2.0 eV.[22] At this point a layer of Na was deposited on the solid NH_3 matrix and the work function was reduced to 1.3 eV. If Na and solid NH_3 were codeposited or deposited in alternating layers then a work function as low as 0.9 (± 0.1) eV was obtained. The fluctuation of ± 0.1 eV came from the variation of the ratio of Na to NH_3 for different runs. The same low work function of 0.9 (± 0.1) eV could also be obtained by codepositing NH_3 with those metals which can be solvated in NH_3 (e.g., Cs, Yb). These results will be published elsewhere.[23]

In conclusion, the double peak structure of the Na $2p$ core level is related to a metal-nonmetal transition. There is clear indication that the higher-binding-energy peak at low coverages is associated with a nonmetallic Na $2p$ core level resulting from the solubility of Na in NH_3. At higher coverages, metallic behavior appears along with a bulk plasmon energy feature. From photoemission investigations, we observe the coexistence of metallic and nonmetallic states in the intermediate range of Na coverage. The relatively large solubility is not predicted by usual extrapolations of the $Na\text{-}NH_3$ phase diagram and can be explained either by an enhanced surface solubility of Na in solid NH_3 or the existence of $Na(NH_3)_x$. In this case, by analogy to the case of Li in ammonia, there would be a regime where $Na(NH_3)_x$ would coexist with the metal and thereby explain the two peak structure.

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