Electronic structure of black SmS. I. $4d$-$4f$ resonance and angle-integrated valence-band photoemission spectroscopy

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We study the electronic structure of single-crystal ''black'' semiconducting SmS using x-ray absorption and resonance photoemission spectroscopy across the $4d$-$4f$ threshold and high-resolution temperature-dependent valence-band photoemission spectroscopy. The $4d$-$4f$ on-resonance spectra show mixed valency of Sm^{2+} and Sm^{3+} states in semiconducting SmS at low temperature ($T=30$ K). The high-resolution spectra show a pseudogap within 20 meV of the Fermi level at low temperatures. This pseudogap is gradually filled up accompanied by a redistribution of spectral weight over a larger energy scale of ~ 200 meV on increasing temperature, resulting in an incipient metallic phase at room temperature. The two energy scales can be associated with the coherence temperature T_c and the Kondo temperature T_K, respectively. The changes in the single-particle density of states at and about the Fermi level are compatible with recent theoretical results on ''exhaustion physics'' in the periodic Anderson model. The present study indicates a Kondo lattice picture for SmS and suggests a relation between the mixed valency and the temperature dependence of the pseudogap for ''black'' semiconducting SmS.

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I. INTRODUCTION

SmS is well known for the first-order pressure-induced semiconductor to mixed-valent-metal transition.[1–3] The low-pressure phase is a black-colored semiconductor possessing rocksalt structure, with a nearly divalent configuration of Sm^{2+} ions corresponding to a $4f^6$ occupancy. The $4f^6$ configuration results in a $J=0$ singlet ground state with the $J=1$ triplet state about 30 meV higher in energy at room temperature. This situation led to SmS being considered a good test example for the mean-field random phase approximation result of an ideal singlet-triplet excitation. In an inelastic neutron scattering experiment done by Shapiro, Birgeneau, and Bucher,[4] the dispersion of the singlet-triplet excitation was traced as a function of temperature and it confirmed the temperature-dependent dynamics of the singlet-triplet model. A clear reduction in the singlet-triplet excitation energy at low temperature compared to the free Sm^{2+} ion was simultaneously observed by Nathan *et al.* using Raman spectroscopy.[5] This was attributed to the exchange interactions which couple neighboring Sm ions and reduces the effective spin-orbit splitting. A similar result was obtained earlier from magnetic susceptibility measurements which showed that SmS exhibits a Van Vleck paramagnetic susceptibility given by $\chi=8N\mu^2/E(T)$, where $E(T)$ is the temperature-dependent singlet-triplet gap and N is the spin density.[6] An admixture of the $4f^5 5d^1$ Sm^{3+} configuration in the ground state was postulated as a reason for the same. Though electron spectroscopy was expected to provide a conclusive answer, early work resulted in conflicting pictures with x-ray photoemission spectroscopy (XPS) indicating less than 3% Sm^{3+} (Ref. 7) while ultraviolet photoemission spectroscopy (UPS) concluding $15\pm 5\%d$ character in the ground state.[8] The presence or absence of $4f^5 5d^1$ Sm^{3+} admixture in the ground state is a necessary input to construct a theory for the pressure-induced transition from black SmS to gold SmS.

The golden-colored high-pressure isostructural metallic phase of SmS exhibits a homogeneous mixed valence as shown by studies of magnetic susceptibility, isomer shift, etc.,[9] with a Sm^{2+} to Sm^{3+} ratio of 7:3. The high-pressure metallic phase is, in fact, qualitatively similar to SmB_6 and YbB_{12} as well as other mixed-valent rare-earth systems including α-cerium.[3,9–12] While gold SmS, SmB_6, and YbB_{12} are actually semiconductors at low temperature and transform to a metal at high temperatures ($\sim$100–150 K), an

important common factor in the mixed-valent metallic state is the so-called Kondo volume collapse relating to a first-order transition with a large volume change, accompanied by a change in the magnetism.[13] The issues of mixed valence and the Kondo effect have retained enormous interest over the years,[14–17] with electron spectroscopy studies playing a significant role throughout, beginning with the work of Allen *et al.*[17] Recent work on the periodic Anderson model (PAM) and the Falicov-Kimball model with new analytic and numeric methods has brought into focus many issues of mixed valence including the connection between the static (e.g., magnetic) and dynamic (such as the density of states) properties of such systems.[18–26] In particular, Tahvildar-Zadeh, Jarrell, and Freericks[18] have shown that their PAM results can account for the dispersion and weak temperature dependence of the Kondo resonance observed in angle-resolved photoemission experiments[27] for a heavy-fermion system. The Kondo resonance at the Fermi level (E_F) of a heavy-fermion metal is due to hybridization of strongly correlated f orbitals with a metallic host, with characteristic high- and low-energy features in photoemission spectroscopy.[14,28–31] The increase of this hybridization then leads to a strongly mixed-valent state. Another group of compounds that fall into the same Anderson lattice class are the Kondo hybridization gap insulators.[32] These can be similarly modeled by one f band hybridizing with a conduction band, with exactly two electrons per unit cell, resulting in a ground-state semiconductor. An important concept put forth by Nozieres[33] and recently gaining more attention for Kondo lattice systems with low carrier density is the relevance of ''exhaustion physics,'' operative when the carriers compensating or screening the local f-electron moments are exhausted. This situation distinguishes collective effects due to the Kondo lattice from the single-impurity problem. Magnetic ordering is suppressed due to quantum fluctuations in this picture. Experimentally, the Kondo insulating behavior is known to be very sensitive to applied magnetic field,[24] pressure,[25] and to a small amount of impurities.[26] It has been shown recently that the width of ''Kondo resonance'' calculated based on the periodic Anderson model and the single-impurity Anderson model gives a measure of the ''coherence temperature T_c'' and the ''Kondo temperature T_K,'' respectively. As a result, there are two energy scales in the problem with T_c suppressed compared to T_K, and this results in a pseudogap below the temperature T_c.[21–23]

In this work, we have studied black semiconducting SmS using high-resolution photoemission spectroscopy as a function of temperature. We used resonant photoemission spectroscopy at low temperature (30 K) across the $4d$-$4f$ threshold on cleaved (100) single-crystal surfaces to reinvestigate the issue of mixed valency in SmS. We have observed features due to Sm^{2+} and Sm^{3+} states at ambient pressure, indicating that black SmS is mixed valent. We confirmed that the relative intensity of the Sm^{2+} and Sm^{3+} states in resonance photoemission spectroscopy (RESPES) is not modified on scraping the surface necessary to obtain the total density of states. We also observed a pseudogap within 20 meV of E_F at 30 K using high-resolution photoemission spectroscopy. The pseudogap gets gradually filled up on increasing temperature to 300 K accompanied by redistribution of spectral weight over a larger energy scale of 200 meV. The changes in the single-particle density of states at and about E_F are compatible with recent theoretical results based on the ''exhaustion physics'' scenario of the periodic Anderson model. The present study thus clearly indicates Kondo lattice effects in SmS.

II. EXPERIMENT

Polycrystalline SmS was first prepared by heating the constituent elements in an evacuated sealed quartz tube. The resulting powder was encapsulated in a tungsten crucible and single crystal SmS was grown by the Bridgman method. The structural, electrical, and magnetic properties have been reported[34] and match well with earlier work.[1–6] X-ray absorption spectroscopy (XAS) and RESPES across the $4d$-$4f$ threshold were performed at beamline 19-B of Photon Factory at Tsukuba. XAS measurements were carried out in the total fluorescence yield mode on cleaved mirrorlike (100) surfaces at $T=30$ K. The base pressure was 5×10^{-10} Torr and the sample surface was stable for a time period of about 40 min. Consequently, the XAS and RESPES spectra on cleaved surfaces reported here were acquired within 30 min of cleaving. The total resolution for the XAS and RESPES measurements was 120 meV at the $4d$-$4f$ threshold. XAS and RESPES spectra were also measured on gently scraped surfaces at 30 K. High-resolution photoemission spectroscopy was carried out at Tohoku University using a SCIENTA SES-200 analyzer and a GAMMADATA discharge lamp with a toroidal grating monochromator. The spectra presented here were recorded with a total energy resolution of 13 meV at 30 K, including the Fermi-Dirac (FD) broadening. The sample surface was gently scraped *in situ* for angle-integrated measurements, ensuring that the surface did not transform to the ''gold'' phase. The scraping was carried out using a diamond file in a base vacuum of 5×10^{-11} Torr for the laboratory measurements. Due to the improved base vacuum and a working pressure of $\sim5\times10^{-10}$ Torr when the discharge lamp is in operation (caused by an increase in He partial pressure monitored using a residual gas analyzer), the sample surfaces were stable for about 1 h. The Fermi level was referred to that of a gold film evaporated onto the sample substrate and its accuracy was better than 0.5 meV. The temperature of sample was measured using a Pt resistor to an accuracy of ±1 K. The spectra were recorded at temperatures between 30 and 300 K, in a temperature cycle, to ensure that temperature-dependent changes were reproducibly obtained.

III. RESULTS AND DISCUSSION

We show in Fig. 1 the valence-band spectra of SmS obtained at 30 K using He Iα ($h\nu=21.218$ eV) or He IIα ($h\nu=40.814$ eV) photons. The He I spectrum shows a three-peak structure between 1 and 3 eV and a broad feature at about 5 eV binding energy with a weak shoulder. The features at 1–3 eV are strongly enhanced in the He II spectrum, suggesting that they are due to Sm $4f$ states. The spec-

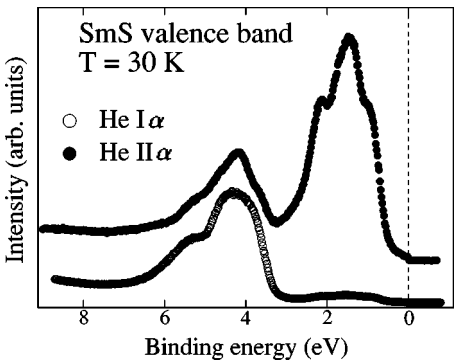

FIG. 1. Valence-band spectra of black SmS measured with He Iα and He IIα photons at $T=30$ K.

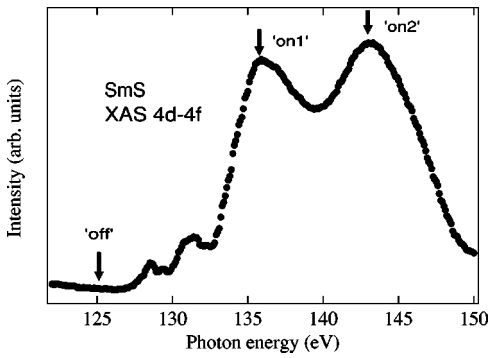

FIG. 2. X-ray absorption spectrum of SmS at $T=30$ K across the $4d$-$4f$ threshold measured in the total-fluorescence-yield mode.

tra are very consistent with earlier valence-band studies on SmS carried out using UPS.[8,35,36] Since the feature at nearly 1 eV binding energy is observed in SmS and not in SmSe, it was assigned to the *d*-derived contribution.[8] However, the three-peak structure between 1 and 3 eV binding energy at low photon energies goes over to a two-peak structure in XPS. This difference is due to an overlap from the surface states (observed only in UPS and shifted to higher binding energy) on the bulk states, which has been proved to be the case by measurements on cleaved surfaces of SmS with oxygen exposure. The oxygen exposure resulted in quenching of the surface states at higher binding energies,[36] similar to that known for Sm metal and SmB_6 (Ref. 37). The bulk states were thus identified to be at 0.8 eV and 1.6 eV binding energy, in very good agreement with XPS valence-band features. Although XPS spectra of substituted SmS (Refs. 7 and 8) and SmB_6 (Refs. 37 and 38) unambiguously show the coexistence of Sm^{2+} and Sm^{3+} features, the general consensus rested at SmS being divalent without a detailed investigation of Sm^{3+} features in black SmS. However, a careful look at the XPS valence-band data of Refs. 7 and 32 shows a broad weak feature centered about 8 eV whose origin has not been discussed in the literature. Since the He I and He II spectra do not show even a weak feature at the same energy in all measurements to date including the present one, we felt it important to confirm states of Sm $4f$ character in SmS. In order to do so, we have carried out XAS and valence-band RESPES across the $4d$ threshold. Due to dipole selection rules, we can thus unambiguously identify $4f$ character in the valence band. We have made an extensive literature survey and to the best of our knowledge there exists only one study of $4d$-$4f$ RESPES of SmS by Gudat *et al.*[39] over a limited photon energy range. We compare and confirm our results with the incident photon energy used in the early measurement and then extend the energy range to identify the $4f$ states in the valence band.

Figure 2 shows the x-ray absorption spectrum measured in the total-fluorescence-yield mode across the Sm $4d$ threshold for a SmS (100) cleaved surface at $T=30$ K. The spectrum is very similar to the constant-final-state spectrum reported earlier.[39] It is well known that the constant-final-state spectrum resembles the x-ray absorption spectrum.[40] We identify prepeaks at 128 eV and 131 eV followed by two main peaks at 135.5 eV and 143 eV, as in the work of Gudat *et al.*[39] We have carried out valence-band RESPES measurements in normal emission at photon energies of 125, 135.5, and 143 eV labeled as "off," "on1," and "on2" in Fig. 2. The RESPES data normalized to the incident photon flux are shown in Fig. 3. The off-resonance spectrum is again very similar to that reported earlier[39] and confirms the quality of the surface. We find a two-peak structure at 0.8 eV and 1.6 eV corresponding to the Sm^{2+} states followed by the S $3p$ derived band at about 5 eV. On increasing the photon energy to "on1," we find a sharp resonant enhancement of the Sm^{2+} features but also weak enhancements of the Sm^{3+} features. The relative intensities at this photon energy do not match with the expected intensities calculated using a fractional parentage method. On tuning the photon energy to "on2," a further enhancement is seen for features due to Sm^{3+} and Sm^{2+} along with changes in the relative intensities of the Sm^{2+} ^6H and ^6F features. The energy positions and relative intensities for Sm^{2+} and Sm^{3+} ions have been calculated using a fractional parentage method[41] and are shown as a bar diagram in Fig. 3. The "on2"-resonance spectra match well with the calculated energy positions for the different multip-

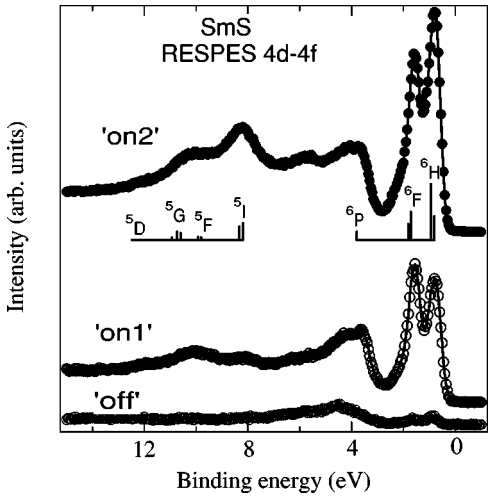

FIG. 3. Resonant photoemission spectra at $T=30$ K across the $4d$ threshold at photon energies labeled "off," "on1," and "on2" in the XAS spectrum in Fig. 2. The bar diagram shows the Sm^{2+} and Sm^{3+} mulitplets calculated using a fractional parentage method (Ref. 41).

lets of Sm^{2+} and Sm^{3+}. Since the ''on2'' measurements are done after the ''on1'' and the relative intensities and energy positions match very well with calculations using a fractional parentage method, we strongly believe the data are intrinsic. The origin of the features is thus well understood as the one-electron removal ^6H, ^6F, and ^6P states of the $4f^6$ configuration of Sm^{2+} and the ^5I, ^5F, ^5G, and ^5D states of Sm^{3+} ($4f^5 5d^1$). The separation between the lowest-energy multiplets of Sm^{2+} and Sm^{3+} is a measure of the on-site Coulomb interaction U_{ff} in SmS and is estimated to be about 7 eV, similar to that obtained in Sm metal and SmB_6 (Ref. 37). The ^6P feature at 4 eV overlaps the broad S $3p$ states centered at 5 eV binding energy. The observation of bulk states in agreement with earlier XPS studies and a suppression of the surface states indicates that RESPES across the $4d$-$4f$ threshold is dominated by the bulk states of Sm $4f$. However, we do not understand the details of the relative intensities of Sm^{2+} and Sm^{3+} and their line shapes in the present case at the intermediate ''on1'' photon energy. Given this complication, it is extremely difficult to extract the relative concentration of Sm^{2+} and Sm^{3+} from the resonant photoemission spectra. The early studies of valence-band RESPES had been carried out up to an incident photon energy of 130 eV. An enhancement of the Sm^{2+} features at an incident photon energy corresponding to the prepeak energy was measured. Further, the change in relative intensities between ''off'' resonance and ''on1'' resonance in the present case are very similar to the data of Ref. 39 measured at 125 eV and 130 eV. In fact, based on a symmetry analysis, it was claimed that resonance enhancement should occur only for the ^6F and ^6P states with the ^6P states showing higher intensity than the ^6F states. The analysis is, however, incomplete, as they have not been measured at higher photon energies. The present study extends the earlier results to RESPES of Sm^{2+}- and Sm^{3+}-derived states occurring at a higher photon energy corresponding to the main peaks observed in XAS and confirms the mixed valency in black SmS. A similar resonance enhancement due to Sm^{2+}- and Sm^{3+}-derived features has been observed for Sm metal and SmB_6 by Allen *et al.*[37] Note that the resonance enhancement is observed only on tuning the photon energy and is not due to a contaminated and degraded surface. We have also measured the ''on2''-resonance spectra of the cleaved surface after degradation as shown in Fig. 4. In comparison with the intrinsic spectrum, we see a sharp decrease in the intensities of Sm^{2+}-derived states after 40 min of cleaving with no enhancement in the intensities of the Sm^{3+}-derived features. However, on scraping the surface with a diamond file, the intensities of the Sm^{2+}- and Sm^{3+}-derived features are remarkably recovered as shown in Fig. 4, although the features are slightly broadened compared to that obtained from cleaved surfaces. We note that since the mixed valency is observed clearly only in the resonantly enhanced spectra, we are unable to quantify the relative contributions of the Sm^{2+}- and Sm^{3+}-derived features in the ground state. However, a pressure-dependent extended x-ray absorption fine structure (EXAFS) study at room temperature reported a valency of 2.1 for SmS in the ambient pressure ''black'' phase which

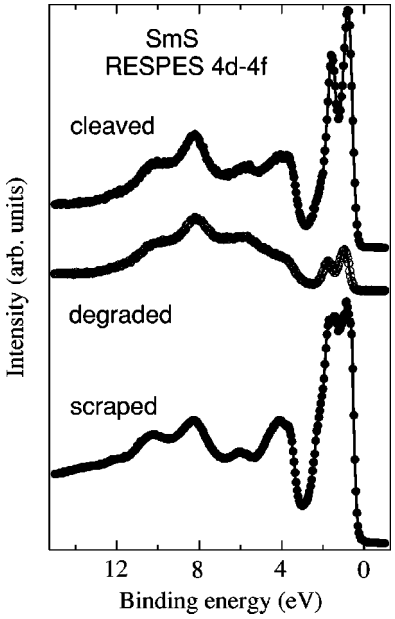

FIG. 4. Resonant photoemission spectra at $T=30$ K across the $4d$ threshold at photon energy ''on2'' to show the intrinsic spectrum for a cleaved surface (upper panel), the degraded spectrum (middle panel), and recovery of the spectral intensity after scraping (lower panel).

increases to about 2.6 in the ''gold'' phase at a pressure of 10 kbar.[42] Another EXAFS study on black SmS, however, considered SmS to be a divalent system but identifies an absorption threshold puzzle: SmS and $Sm_{1-x}Y_xS$ exhibit the same threshold in spite of the mixed valency of $Sm_{1-x}Y_xS$.[43]

Figure 5 shows the valence-band spectrum of SmS at 300 K superimposed on the 30 K spectrum obtained using He II radiation for scraped surfaces. The spectrum at 300 K clearly shows that the Sm^{3+} features increase in intensity while the Sm^{2+}-derived features weaken compared to the 30 K spectrum. However, such a behavior is also expected to appear due to contamination and oxidation of the surface at higher temperatures, though we do not see changes up to 1 h after scraping in a base vacuum of 5×10^{-11} Torr. Unfortunately,

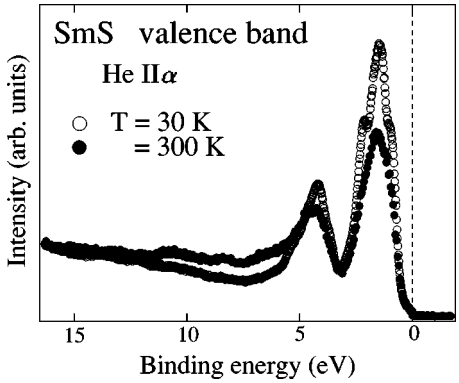

FIG. 5. He II valence-band spectrum of black SmS at 30 K compared to that at 300 K, showing the growth of Sm^{3+} features and a reduction of Sm^{2+} features. The spectra are normalized to the integrated intensity.

we were not able to measure the $4d$-$4f$ RESPES at high temperatures because of the poorer vacuum (5×10^{-10} Torr) and the rapid degradation of surface. Thus, the present temperature-dependent observations are only suggestive of possible changes in mixed valency as a function of temperature in black SmS. A similar behavior using temperature-dependent XPS is known for the collapsed phase of mixed-valent metallic $Sm_{0.81}Y_{0.19}S$ and $SmAs_{0.18}S_{0.82}$ (Ref. 44).

The above experimental results and assignment of features are consistent with recent theoretical calculations of the electronic structure of SmS.[45–49] Most significantly, it has been shown recently by Strange *et al.*[47] from a first-principles calculation that the mixed-valence transition in Sm chalcogenides is not a transition starting with an integer number of localized f states. Rather, the system undergoing a mixed-valence transition as a function of a physical parameter actually exhibits a transition between two states both with a nonintegral number of delocalized f electrons and an integral number of localized f electrons. The difference in energy of the Sm^{2+} and Sm^{3+} configurations has also been calculated[45] from a total energy method and is of the order of 15 meV for SmS, which is of the scale of room temperature. These theoretical studies also reproduce the intricate valence stability and the systematics observed in various properties of mixed-valent Sm, Eu, Tm, and Yb compounds.[45–48] It was also shown using a multiband periodic Anderson model for SmS within the local density approximation[49] that the semiconducting ''black'' phase also has a small amount of mixed valency which increases in the ''gold'' phase. In the following paper, we report our angle-resolved photoemission spectroscopy on SmS at $T=30$ K, which determines the experimental band structure. Comparison of the experimental result with the local density approximation (LDA) band calculation is presented.

The existence of mixed valency naturally gives rise to the question of changes in the spectra at and near E_F, as is known for other Ce- and Yb-based Kondo systems.[31,50] In Fig. 6(a), we plot the near-E_F spectra of SmS obtained using He II radiation at 30 and 300 K normalized to the area under the curve up to 300 meV binding energy. The spectrum at 30 K clearly shows two features: one at about 30 meV and another broad feature centered at about 160 meV. Due to the low intensity at and near E_F in UPS spectra and the inadequate resolution used in earlier studies, these features have not been clearly identified. Going back to the RESPES spectra obtained at the ''on2'' resonance (Fig. 3), since the spectra do not show enhancement near E_F, these features cannot be said to have $4f$ character. Further, while the energy of these features agrees well with the electronically active modes for SmS corresponding to the $J=0$ to $J=1$ and 3 of the ^7F_J multiplets as identified from Raman spectroscopy,[5,51] the absence of a feature for $J=0$–2 indicates a different origin for these features. In order to see the changes in the density of states (DOS) we have divided the raw spectra by the Fermi-Dirac function at the relevant temperature convoluted with a Gaussian for the experimental resolution. The result is shown in Fig. 6(b). We see a clear pseudogap in the DOS at 30 K within 20 meV of E_F. This pseudogap is filled

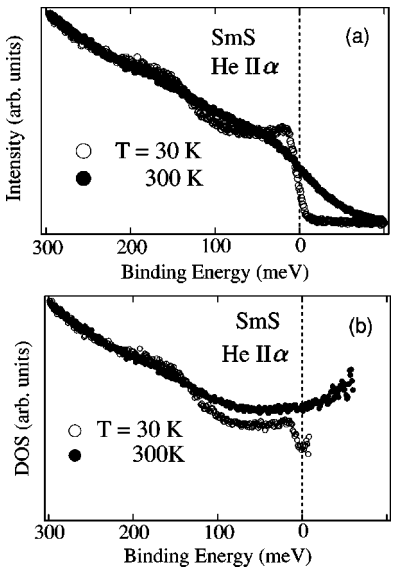

FIG. 6. (a) Raw He II spectra near E_F of SmS measured at 30 and 300 K. (b) He II spectra after dividing by the Fermi-Dirac function convoluted by a Gaussian for the experimental resolution. A low-energy (20 meV) pseudogap at $T=30$ K is clearly observed, which gets filled up at 300 K, accompanied by spectral changes up to about 200 meV.

up at 300 K accompanied by a redistribution of the spectral weight over 200 meV as clearly seen in Fig. 6(a). In order to check the observed behavior, we have measured near-E_F spectra with high resolution as a function of temperature. Figure 7(a), shows the spectra obtained with He I radiation from 30 to 300 K. The spectra show weaker intensity features compared to that observed in He II spectra, but at identical energy positions. The weaker intensity in He I spectra compared to He II spectra and the absence of f character in the RESPES measurements at or near E_F (Fig. 3) indicate the d character of these states. As a function of temperature, a systematic reduction in the spectral features is observed on increasing temperature, with a simultaneous increase in the DOS at E_F. The same analysis of dividing by the Fermi-Dirac function convoluted with a Gaussian confirms the pseudogap behavior and a gradual filling up of the same on increasing temperature as shown in Fig. 7(b).

A similar observation of the pseudogap with a gradual filling up is known for other Kondo insulators: $Ce_3Bi_4Pt_3$ (Ref. 52), YbB_{12} (Ref. 53), CeRhSb, and CeRhAs (Ref. 54). In fact, SmS has also been classified as a Kondo insulator from thermodynamic studies.[32] Comparing with other experimental data on SmS, the value of the pseudogap observed in the present measurement is much smaller than that estimated from the optical study[1] ($\sim$200 meV) or the electrical resistivity measurement[34] below 150 K ($\sim$100 meV). Resistivity studies indicate a deviation from an activation type above 150 K. As pointed out by Varma,[3] pure SmS should also exhibit a semiconductor-to-metal transition from early resistivity data of Bader *et al.*[2] as a function of pressure at specific temperatures. In particular, their data at 473 K indicate a metallic phase at ambient pressure, while the low-

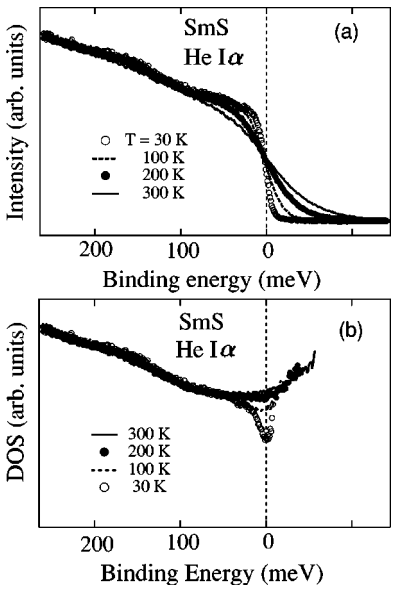

FIG. 7. (a) Raw He I spectra near E_F of SmS measured at 30 and 300 K. (b) He I spectra divided by the Fermi-Dirac function convoluted by a Gaussian as in Fig. 6, confirming a pseudogap below 20 meV and spectral changes up to 200 meV. A gradual increase in the DOS at E_F results in an incipient metallic phase by 300 K.

temperature phase is semiconducting. The photoemission spectra for temperatures at and above 200 K show a leading edge identical with that of gold, indicating an incipient metallic phase. Further, the present study provides two energy scales in the electronic structure of SmS which can be associated with the ''coherence temperature T_c'' (20 meV to 200 K) and the ''Kondo temperature T_K'' (200 meV to 2000 K), respectively. This is in agreement with calculations of the single-particle density of states for the periodic Anderson model in the ''exhaustion'' limit and is similar to observations on other Kondo insulators discussed above. Thus, the results of the spectral changes at and about E_F seem most compatible with the spectra calculated for a low-carrier Kondo lattice system displaying two energy scales.[21–23] The fact that the spectral features are not due to multiplet excitations known for this system indicates a different origin to the observed features. In conjunction with known results of optical[55] and point contact spectroscopy[56] for gold SmS, which concluded a high f-f spectral density at low-energy scales (<25 meV) and RESPES, which indicates more d DOS within 25 meV of E_F in the occupied DOS, the following picture is suggested for black SmS: the $4f$-derived states are away from E_F with a small amount of $5d$ states closer to E_F in the valence band due to the mixed valency. On transforming to gold SmS, the $4f$ states move closer to E_F, overlapping the $5d$ states along with an increase in mixed valency. It would be important to study higher-resolution temperature-dependent RESPES to identify d-character states in the valence band of SmS and the interplay of d and f states, particularly near E_F. Such studies are beyond our scope presently and synchrotron-radiation measurements with improved intensity and resolution would be able to realize this possibility.

IV. CONCLUSIONS

The $4d$-$4f$ on-resonance spectra show mixed valency of Sm^{2+} and Sm^{3+} states in semiconducting SmS, which precedes the Kondo volume collapse. This could be a characteristic of Kondo insulators and has been discussed earlier.[57] We have identified two energy scales in SmS using high-resolution photoemission spectroscopy, which are associated with the ''coherence temperature T_c'' causing a low-energy (20 meV) pseudogap and the ''Kondo temperature T_K'' (200 meV), respectively. The pseudogap is gradually filled up on increasing temperature accompanied by spectral weight redistribution over 200 meV. The present work indicates Kondo lattice effects in SmS and suggests a relation between mixed valency and the temperature dependence of the pseudogap.

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