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Strong Correlation Effects in the (3 × 3) Charge Density Wave Phase of Sn/Ge(111)

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Angle resolved photoemission spectra of Sn/Ge(111)-α phase show a transition from a dispersive state at 295 K in the metallic $(\sqrt{3} \times \sqrt{3})$ phase to a state with negligible momentum dispersion in the (3 × 3) charge density wave (CDW) phase at 110 K. A depletion of density of states at the Fermi level is observed in photoemission and electron energy loss spectra at 110 K. These effects and the splitting of the Sn p_z band at 110 K point to correlation effects as the cause of the transition to the CDW state. [S0031-9007(97)04382-2]

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Several surface adsorbate phases (e.g., Pb/Ge(111) (3 × 3) [1–3], K/Si(111)-$(\sqrt{3} \times \sqrt{3})R30°$-B [4], 6H-SiC(0001) $(\sqrt{3} \times \sqrt{3})$ [5]) which have an odd number of surface electrons in their unit cell, and therefore should be metallic in a simple band picture, are instead insulating according to photoemission or electron energy loss spectra. These surfaces have similar T_4 adatom structures in a triangular lattice with relatively long distances between adatoms dangling bonds (5.4–7 Å). Appreciable correlation effects are expected in the half-filled dangling-bond derived band, since its dispersion is comparable to the estimated Coulomb repulsion U between electrons on a lattice site (0.5–2 eV) [4,6]. A nice example of these effects is provided by the K/Si(111)-$(\sqrt{3} \times \sqrt{3})R30°$-B surface, whose photoemission and inverse photoemission spectra have been recently interpreted in terms of a two-dimensional Mott-Hubbard insulator [4]. These overlayers form a class of systems in which correlation effects in a two-dimensional electron liquid can be studied with all the available surface science techniques and in which the electron density and the degree of long range structural order can be varied.

The α phases of Pb/Ge(111)-$(\sqrt{3} \times \sqrt{3})$ and of Sn/Ge(111)-$(\sqrt{3} \times \sqrt{3})$ show a transition from a normal metallic phase to a commensurate charge density wave (CDW) state below 250 and 210 K, respectively [1,7]. In the case of Pb/Ge(111), this transition has been reported to be accompanied by the opening of a gap at the Fermi level a few tens of meV wide [1–3]. It has been proposed that the transition to the low temperature CDW state is driven by the nesting of the Fermi surface [1], and a Fermi surface vector of the right magnitude has been reported [3]. However, new local density approximation (LDA) calculations for Sn/Ge(111)-α phase [6,7] indicate that Fermi surface nesting does not play a role in the $(\sqrt{3} \times \sqrt{3}) \rightarrow (3 \times 3)$ transition. The calculated nesting vector is larger than the ΓK distance, i.e., the value that would give rise to the commensurate (3 × 3) CDW. Therefore, the relevance of the Fermi surface nesting and the role played instead by correlation effects in the transition from the normal metallic state to the surface CDW state is an open question.

Angle resolved photoemission spectroscopy can provide experimental data on the Fermi surface of these systems and on the one-electron spectral distribution $A(k, \omega)$ in the normal and in the CDW phase, that contains the information on the correlation effects in the electronic structure of the systems. Low energy electron diffraction (LEED) and scanning tunneling microscopy data (STM) indicate that the structure of the Sn overlayer is only weakly perturbed by the 210 K transition [7], therefore changes in the photoemission spectra can be attributed to correlation effects if also the substrate is weakly affected. Moreover, the Sn/Ge(111) $(\sqrt{3} \times \sqrt{3})$ and (3 × 3) surfaces can be easily grown with low density of defects [8], contrarily to the case of Pb/Ge(111), making the application of the angle resolved photoemission technique to this surface fully meaningful. In this Letter we present angle-resolved photoemission spectra and electron energy loss spectra (EELS) of the surface states of Sn/Ge(111) that brings out appreciable many body effects in the CDW state.

Sn was dosed onto a n-type Ge(111) substrate (Sb doped, 0.1 Ω cm) at room temperature and the coverage θ was estimated by Auger spectroscopy [9] and LEED. The (3 × 3) phase can be observed by LEED for θ between 0.28 monolayer (ML) ($1\ \mathrm{ML} = 7.21 \times 10^{14}$ atoms cm^{-2}) and 0.43 ML in samples annealed between 480 and 570 K and then cooled below 200 K. The sharpest (3 × 3) LEED pattern was observed at about 0.35 ML and at 110 K. The (3 × 3) LEED pattern transforms into a $(\sqrt{3} \times \sqrt{3})$ gradually and reversibly when the temperature is raised above 200 K. This pattern is stable up to 550 K. The angle resolved photoemission spectra were measured by a hemispherical analyzer with an energy resolution of 40 meV and an angular acceptance of ±1° ($\Delta k \pm 0.03$ Å^{-1}) with 21.2 eV photons (He I) at an incidence angle of ~20°. Spectra taken with an angular acceptance of ±0.4° are similar to those reported in this Letter. The Fermi level was measured with an error of ±5 meV taking spectra of the Ta sample holder and of 2.5 ML Sn films grown on the same Ge(111) substrate. The EEL spectra were measured with a Leybold-Hereaus ELS-22 spectrometer set to an energy resolution of 15 meV.

The dispersion of the Sn p_z derived surface state is evident in the 295 K photoemission spectra shown in Fig. 1. According to the LDA calculations [7] the Sn dangling bond band is above the Fermi level E_F at Γ, crosses E_F midway between Γ and K and goes about 0.3 eV below E_F at K. In agreement with the calculations our 295 K photoemission spectra show a ~0.4 eV broad peak that is absent near Γ, has a maximum at a binding energy (B.E.) of 0.1 eV when the parallel wave vector q is 0.3–0.4 $\mathrm{\AA}^{-1}$ and shifts at 0.3 eV below E_F at K ($q = 0.61$ $\mathrm{\AA}^{-1}$). The lower panel of Fig. 1 shows the dispersion of the Sn induced band obtained by plotting the energy of the maximum of the Sn induced peak (circles) or by fitting the spectra with Gaussians and a linear background multiplied by the Fermi distribution function (squares). The extrapolation of these data to the Fermi level gives a Fermi wave vector of 0.2–0.3 $\mathrm{\AA}^{-1}$ at 295 K.

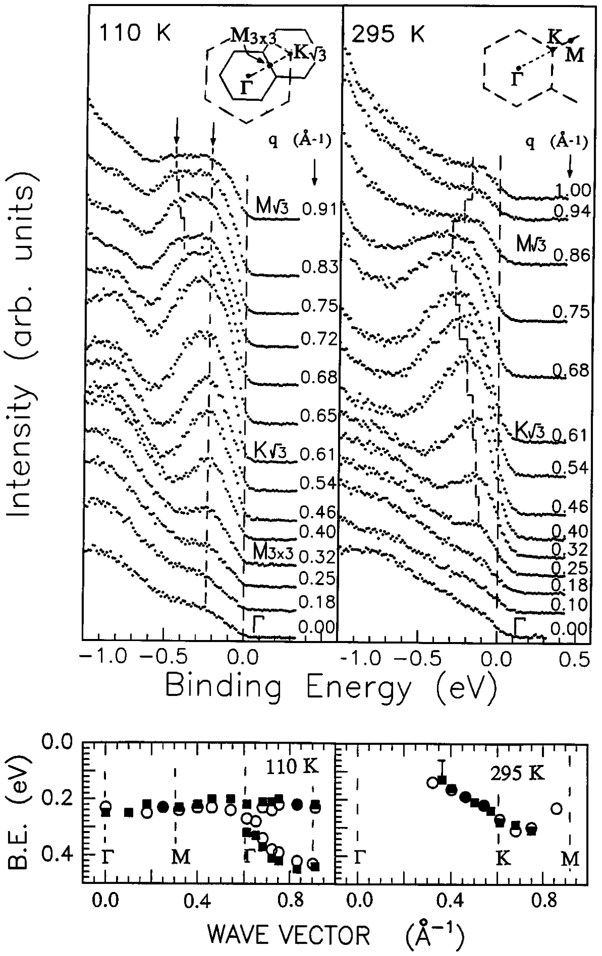

FIG. 1. Upper panel: Photoemission spectra of the $(\sqrt{3} \times \sqrt{3})R30°$ (295 K) and of the (3×3) phase of Sn/Ge(111) at 110 K as a function of the parallel momentum q along the ΓK direction of the $(\sqrt{3} \times \sqrt{3})R30°$ Brillouin zone. This zone and that of the (3×3) structure are shown by dashed and by solid lines, respectively, in the upper part of the figure. The values of q refer to electrons with 0 eV B.E. Lower panel: Dispersion of the Sn peak (see text).

In contrast to the 295 K results, the spectra of the sample in the (3×3) CDW phase at 110 K show a peak at a constant binding energy (0.23 eV) from Γ to K and M, while a second structure with a 0.15 eV dispersion appears close to the edge of the $(\sqrt{3} \times \sqrt{3})$ Brillouin zone at about 0.4 eV B.E. A Gaussian peak at 0.23 ± 0.03 eV is necessary to fit the lowest B.E. structure in the whole range of q. These results are in contrast with the LDA calculations of Sn/Ge(111)-α phase [6,7], according to which the $(\sqrt{3} \times \sqrt{3})$ structure is stable against the (3×3) reconstruction at low T and the band structure does not depend on temperature. According to these calculations, appreciable dispersion should be observable also at 110 K. A stable (3×3) phase at low temperature has been found by LDA calculations for Pb/Ge(111)-α phase [1]. The calculated low temperature band structure of this system is very similar to that obtained by simply folding back the band structure of the 300 K $(\sqrt{3} \times \sqrt{3})$ phase and does not show any adatom induced band between 0.05 and 0.6 eV for $q > 0.2$ $\mathrm{\AA}^{-1}$. Therefore the negligible dispersion of the Sn derived 0.23 eV peak and the second peak at 0.4 eV cannot be explained either by the Sn/Ge(111) or by the Pb/Ge(111) calculations. The Sn/Ge(111) spectra are in agreement with the LDA calculations only in the normal $(\sqrt{3} \times \sqrt{3})$ phase. The large difference in dispersion between 295 and 110 K indicates that while the electrons in the Sn p_z band are delocalized in the $(\sqrt{3} \times \sqrt{3})$ phase, they become strongly localized in the (3×3) CDW phase. This fact, and the presence of the second band at 0.4 eV, emphasize the importance of the electron correlation in this system.

The linewidth of the surface state in the photoemission spectra is quite large, the full width at half maximum is about 0.3 eV at 110 K and between 0.3 eV ($q = 0.3$ $\mathrm{\AA}^{-1}$) and 0.6 eV ($q = 0.7$ $\mathrm{\AA}^{-1}$) at 295 K, according to the fits with Gaussians. It is comparable to that observed in another strongly correlated surface system, K/Si(111)-$(\sqrt{3} \times \sqrt{3})R30°$-B [4]. A Gaussian Frank-Condon envelope caused by the excited phonons of the localized positive-ion final state is a plausible explanation for the large width [4]. If phonon excitations in the final state are the cause of the broadening they should also shift the photoemission peak [10]. Therefore the binding energy of the surface state can be appreciably less than that indicated by the maximum of the photoemission peak and the value of the Fermi wave vector obtained from the band dispersion (lower panel of Fig. 1) may be underestimated.

Similarly to the case of Pb/Ge(111) [2], the photoemission intensity at the Fermi level I_F decreases by about a factor of 2.5 when the temperature is lowered to 110 K (Figs. 1 and 2). This effect is not due to surface photovoltage or charging of the sample since other sharp structures of the photoemission spectrum (not reported in Fig. 1) do not shift to higher binding energy when the temperature is lowered. Moreover, the Fermi edge of 2.5 ML Sn films

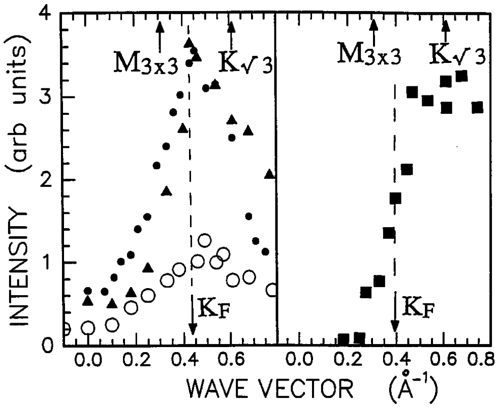

FIG. 2. Photoemission intensity at the Fermi level I_F at 295 K (filled circles) and at 110 K (empty circles), slope of the low binding energy side of the Sn induced peak (triangles) and intensity of the Sn induced peak at 295 K (squares) as a function of q along the ΓK direction.

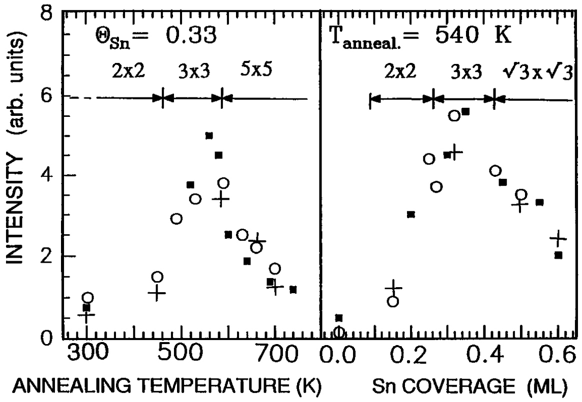

FIG. 3. Photoemission intensity at 0.2 eV (circles), at the Fermi level at 110 K (crosses) and HREELS intensity at 0.2 eV (squares) as a function of Sn coverage (right panel) and annealing temperature (left panel). The ranges in which the (2×2), (3×3), $(\sqrt{3} \times \sqrt{3})R30°$, and (5×5) LEED patterns are observed at 110 K are also shown.

grown on the same Ge substrate does not shift with temperature within 5 meV. The decrease of the intensity at the Fermi level is therefore caused by a strong depletion of density of states at E_F in the CDW phase. Figure 2 shows the wave vector dependence of I_F along ΓK (filled circles). The maximum is reached at $q = 0.43 \pm 0.03$ Å^{-1} at 295 K. The same figure also shows the maximum slope of the low B.E. side of the Sn induced peak (triangles) and the integrated intensity of the same structure at 295 K (squares), measured by fitting the spectra with Gaussians, as a function of q. Our experimental energy resolution, 40 meV, is much less than the intrinsic width of the photoemission peaks. Therefore the crossing of the Fermi level of the Sn band should be marked by the maximum of I_F, the maximum of the slope of the spectra in the 0.1–0 eV B.E. region [11] and the point at half height in the integrated intensity data. All these criteria give a Fermi wave vector along ΓK of 0.43 ± 0.04 Å^{-1}, while the value necessary to explain the CDW transition as an effect of the nesting of the Fermi surface is 0.30 Å^{-1} [1]. These results are in agreement with those obtained for Pb/Ge(111) by us [2], but in contrast with those of the Madrid group [3] and with the Fermi wave vector estimated from the band dispersion in Fig. 1. We believe that the discrepancy between the value obtained from the band dispersion and that obtained from the data of Fig. 2 comes from the broadening and the shift of the Sn p_z photoemission peak caused by electron-phonon and electron-electron interaction. Because of these effects the energy of the maximum of the photoemission peak may overestimate the binding energy of the p_z states and the Fermi vector deduced from Fig. 1 may be underestimated.

We have checked if the measured spectra were those of the $(\sqrt{3} \times \sqrt{3})$ and (3×3) phases and if contributions from other phases were present. Figure 3 shows the intensity of the 0.2 eV photoemission peak as a function of Sn coverage and annealing temperature T_a. The intensity of the 0.4 eV peak follows the same behavior. These intensities have a maximum when θ and T_a are those that give the best $(\sqrt{3} \times \sqrt{3})$ and (3×3) LEED patterns at 295 and 110 K, respectively, while they are strongly quenched when other phases, indicated in Fig. 3, are present. None of these phases has photoemission peaks between 0 and 0.5 eV.

The depletion of density of states at the Fermi level in the low temperature CDW phase indicated by the photoemission data can be checked by measuring the electron energy loss spectrum. The EELS of the (3×3) phase is shown in Fig. 4 and compared to that of the same sample

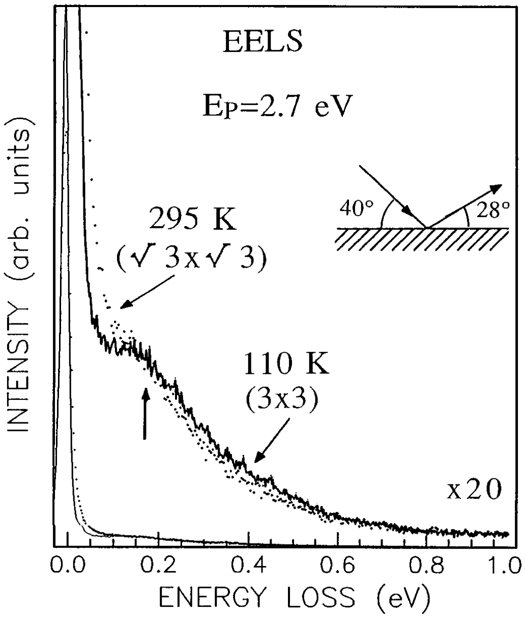

FIG. 4. Electron energy loss spectra of the normal (295 K) and of the CDW (110 K) phase of Sn/Ge(111) measured in the off specular scattering geometry shown in the upper part of the figure. Note the decrease of the scattering cross section below 150 meV and the broad hump at about 200 meV in the (3×3) CDW phase.

in the $(\sqrt{3} \times \sqrt{3})$ phase at 295 K. There is a clear decrease of the scattering cross section at energies lower than 150 meV and an increase between 150 and 600 meV when the temperature is lowered to 110 K. This again indicates that the density of states is appreciably depressed near the Fermi level in the CDW state and that the spectral weight of the electronic excitations moves to higher energies. The EELS is similar to that of the Pb/Ge(111) (3×3) surface [1], but in our case the structure at about 0.2–0.3 eV is less prominent. The 0.2 eV hump is present in the spectra measured in scattering geometries that maximize the sensitivity to impact scattering, i.e., off specular geometry. Its intensity has a sharp maximum at low primary electron energies (3–3.8 eV) and becomes quickly negligible at higher primary energies. The associated electronic transitions are therefore dipole forbidden [12] and may be excited by exchange scattering. When the sensitivity to dipole scattering is maximized (specular geometry), only a metallic Drude tail of the elastic peak is observed up to 0.6 eV, the intensity of which decreases by a factor of 2.5 between 295 and 110 K. The intensity of the 0.2 eV EELS hump follows closely the coverage and annealing temperature dependence of the Sn p_z photoemission peak, having a maximum when the (3×3) LEED pattern is strongest (Fig. 3, squares). Therefore the 0.2 eV structure belongs to the (3×3) CDW phase.

The CDW phase of Sn/Ge(111) is still metallic since the (3×3) photoemission spectra show appreciable intensity at E_F, and the specular EELS shows a metallic Drude-like tail even at 110 K. The photoemission intensity at E_{F} at 110 K is higher in the (3×3) phase than in the other phases [disordered, (2×2), (5×5), $(\sqrt{3} \times \sqrt{3})$ at higher coverages] by at least a factor of 2 (see Fig. 3). Therefore the residual intensity of the (3×3) phase is not due to regions of the sample that are in another phase. Both photoemission and EELS indicate a decrease of the density of states at E_{F} by a factor 0.4 ± 0.1 with respect to the 295 K phase. The calculated LDA band structure of Sn/Ge(111)-α phase [7] does not depend on temperature and that of Pb/Ge(111)-(3×3) [1] is nearly identical to that obtained by folding back the $(\sqrt{3} \times \sqrt{3})$ band. Therefore these calculations, providing the same density of states at low and at high temperature, do not explain the effects observed at E_{F}. Some of the states removed from the Fermi region are shifted to higher binding energy (0.2 eV), in particular in the central part of the Brillouin zone, according to the photoemission data. The spectrum of the electronic excitations from the filled to the empty adatom states is about 0.6 eV wide, with a maximum at 0.2 eV (Fig. 4). Therefore the experimental data indicate that correlation effects in the low temperature CDW phase tend to split the surface Sn derived band into two subbands separated by ~0.2 eV or more. The splitting measured by EELS may be less than the separation of the subbands because of excitonic effects [4]. This splitting is not complete since the density of states at E_{F} does not vanish.

Model Hartree-Fock, local spin density approximation, and Lanczos calculations for this type of surface phase [6] predict a reduced density of states at E_{F} and a spreading of bands 0.2–0.6 eV below the Fermi level. The bands are neatly split, as in our 110 K spectra, if the amplitude of the commensurate surface charge density wave is large. These theoretical results are consistent with the observed photoemission and EELS spectra.

In conclusion, the negligible dispersion of the Sn band in the CDW state indicates electron localization and therefore important correlation effects in the (3×3) CDW phase of Sn/Ge(111). This is also confirmed by a strong depletion of spectral weight at E_{F} with respect to the room temperature data and by the splitting of the filled Sn band.

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