

## Critical behavior of the plasmon resonance at the metal-insulator transition in VO<sub>2</sub>

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A large red shift in the energy of the plasmon resonance in metallic VO<sub>2</sub> has been observed by decreasing the temperature near the metal-to-insulator phase transition ( $T_c = 68^\circ\text{C}$ ). Below the transition temperature the plasmon resonance disappears. The plasmon resonance has been studied from thermorefectance spectra of an oriented single crystal. Polarized spectra varying the crystal temperature have been recorded. This experiment gives direct evidence that the metal-insulator transition in VO<sub>2</sub> is a Mott-type transition from delocalized conduction states to localized states on the V-V dimers.

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### I. INTRODUCTION

The physical explanation of the metal-insulator phase transition (MIT) of VO<sub>2</sub> and of various transition-metal oxides has been the object of extensive experimental and theoretical investigation in these last years, after the first experiment of Morin.<sup>1</sup> A conductivity jump of a factor as large as  $10^5$  appears at  $T_c = 68^\circ\text{C}$  as the VO<sub>2</sub> crystal undergoes a transition from the high-temperature metallic phase to the low-temperature semiconducting phase.

The transition is first order with an entropy change  $\Delta S = 3 \text{ cal/mol K}$ .<sup>2</sup> A band gap of  $\Delta E = 0.6 \text{ eV}$  has been found in the semiconducting phase from transport,<sup>3</sup> optical,<sup>4,5</sup> and photoemission experiments.<sup>6</sup> The transition is accompanied by a structural phase transition<sup>7,8</sup> from a tetragonal high-temperature form to a monoclinic low-temperature form. The high-temperature "rutile" form is characterized by chains of equidistant vanadium atoms ( $d_{V-V} = 2.86 \text{ \AA}$ ) along the rutile  $c_r$  axis. This distance is anomalously short in comparison with expected interatomic metal-metal distance between the V<sup>4+</sup> ions deduced from the trend of interatomic distances in  $3d$  transition-metal oxides with rutile structure ( $d_{V-V} = 2.95 \text{ \AA}$ ).<sup>8</sup> In the monoclinic form the V-V distances alternate between longer and shorter distances forming a zig-zag chain along the monoclinic  $a$  axis corresponding to the rutile  $c_r$  axis.

The controversy is about the role of electronic and lattice contributions to the MIT in VO<sub>2</sub>. The MIT has been assigned by some authors to a Mott-type transition driven by intraelectron correlations,

by others to a charge-density-wave type of transition, and by still others it was associated with a contingent opening of a band gap due to the change of crystal periodicity. Moreover, the Mott-type MIT of VO<sub>2</sub> is not a characteristic Mott transition where the electrons of a highly correlated electron gas become localized by a short-range Hubbard repulsion energy  $U$ , but it has been described rather as driven by intraelectron correlations of the Heitler-London-type.<sup>9</sup> In fact, in semiconducting VO<sub>2</sub>, the electrons become localized in the V-V dimers,<sup>10</sup> and the correlated state of electrons in the  $d_{x^2-y^2}$  orbitals of a pair of vanadium atoms could be described by diamagnetic Heitler-London wave functions.

For each material which exhibits an MIT transition an accurate theoretical experimental study is necessary to decide the type of transition. The importance of electron correlation on V<sub>2</sub>O<sub>3</sub> has been demonstrated by Castellani, Natoli, and Ranninger.<sup>11</sup> On the contrary, the MIT transition of Ti<sub>2</sub>O<sub>3</sub> is due to structural-induced band decrossing.<sup>12,13</sup>

The role of electron correlation in VO<sub>2</sub> has been emphasized in the theoretical work by Zylbersztein and Mott in their review of the electronic properties of VO<sub>2</sub> (Ref. 14) and by Sommers *et al.*<sup>9</sup> Other authors<sup>2,15</sup> have assigned the VO<sub>2</sub> MIT mainly to the structural phase transition. A recent theoretical calculation has suggested that the MIT driving mechanism is the formation of a charge-density wave.<sup>16</sup> Therefore more experimental work which could separate the effects of lattice distortion from that of electron localization is required to clarify the mechanism of MIT in VO<sub>2</sub>.

We have studied the behavior of the plasmon resonance in  $\text{VO}_2$  as a function of crystal temperature. Polarized thermoreflectance spectroscopy of a single crystal is one of the best methods used to study the plasmon resonance. Thermoreflectance spectra show a strong negative minimum at the plasmon resonance which can be easily analyzed.<sup>13</sup> The theory of plasmons in a narrow  $d$  band, as in transition-metal oxides, has been developed recently.<sup>17</sup> The effect on the plasmon energy of the band-gap opening at the metal-to-insulator transition has been calculated.<sup>17</sup>

The plasmon resonance has already been studied in two crystals:  $\text{Ti}_2\text{O}_3$  (Ref. 17) and  $2H\text{-TaSe}$  (Ref. 18) where the band gaps and plasmon energies are similar to  $\text{VO}_2$ , but where the MIT is due to a "band crossing" induced by the structural distortion, and to charge-density-wave mechanism, respectively. In agreement with theory,<sup>17</sup> the effect of the band-gap opening on the plasmon energy is only a small blue shift with decreasing temperature.

In  $\text{VO}_2$  we have found quite a different plasmon behavior from  $\text{Ti}_2\text{O}_3$  and  $2H\text{-TaSe}$ . We explain this behavior as evidence of localization of conduction electrons due to electron-electron interaction. Moreover, we suggest a model of "interconfiguration fluctuations" for metal  $\text{VO}_2$ .

## II. EXPERIMENTAL

The sample was a  $\text{VO}_2$  single crystal characterized by x-ray diffraction. The single crystal was cut so that the  $c_r$  axis of the rutile phase was parallel to the surface plane. Polarized thermoreflectance spectra with the electric-field vector  $\vec{E}$  parallel and perpendicular to the  $c_r$  axis were recorded. The details of the apparatus were reported in Ref. 13.

The  $\text{VO}_2$  temperature was modulated by keeping a small thin sample in thermal contact with a thin long graphite slab. The electric current in the graphite slab was modulated at a frequency of 1 Hz. The peak-to-peak amplitude of crystal temperature modulation was found to be about 1 K. The sample temperature was measured by a thermocouple on the sample but this measure can be affected by a systematic error due to temperature gradients or thermal contacts. The temperature, where a sharp decrease of reflectivity signal due to phase transition appears, has been taken to be  $68^\circ\text{C}$ , in agreement with previous measurements.<sup>5</sup> This temperature has been used in this work as the transition temperature  $T_c$ .

## III. RESULTS

Figure 1 shows the polarized  $\vec{E} \perp c_r$  thermoreflectance spectra at several temperatures above and below the metal-to-insulator transition (MIT) temperature  $T_c$ . The plasmon resonance appears in the spectra of the metal  $\text{VO}_2$  as the characteristic negative peak at 1.65 eV.<sup>13</sup> By decreasing the temperature toward the transition temperature, the intensity of this peak becomes very large, and at 1 K above  $T_c$  the measured plasmon frequency is 1.22 eV. At 1 K below  $T_c$  the plasmon disappears. Owing to

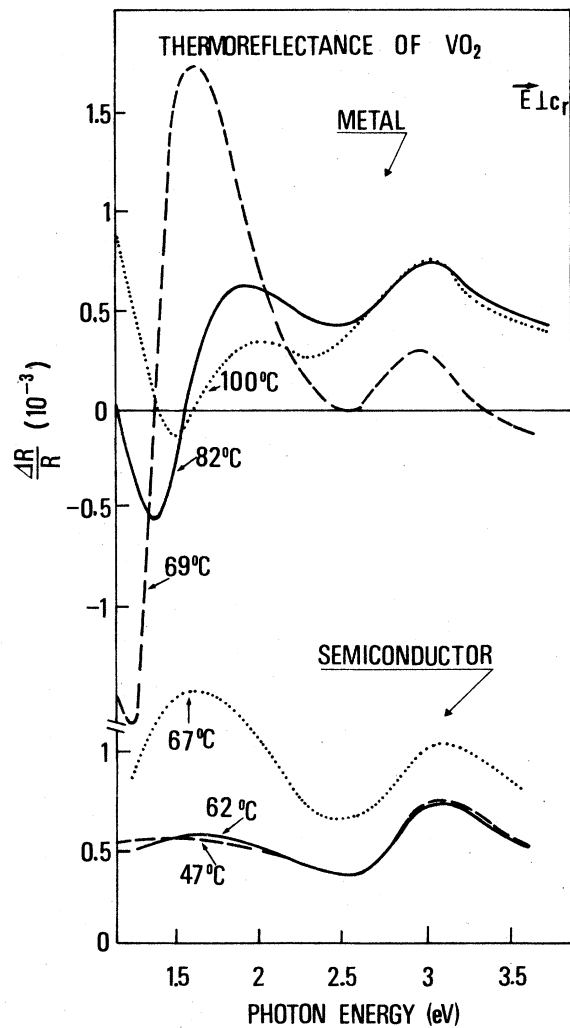


FIG. 1. Thermoreflectance spectra of  $\text{VO}_2$ , using polarized light  $\vec{E} \perp c_r$ , as a function of the crystal temperature. In the upper part of the figure the spectra of the metal phase are plotted. In the lower part, the spectra of the semiconducting phase, below  $68^\circ\text{C}$ , show that the minimum at 1.2–1.6 eV due to plasmon resonance, disappeared.

the amplitude of temperature modulation of the sample we were not able to further approach the transition temperature. The structure at 2.9 eV is practically unaffected by the MIT. Figure 2 shows the polarized  $\vec{E}||c_r$  thermorefectance spectra of metal VO<sub>2</sub>. The same temperature dependence of the plasmon resonance has been found in the  $\vec{E}\perp c_r$ ,

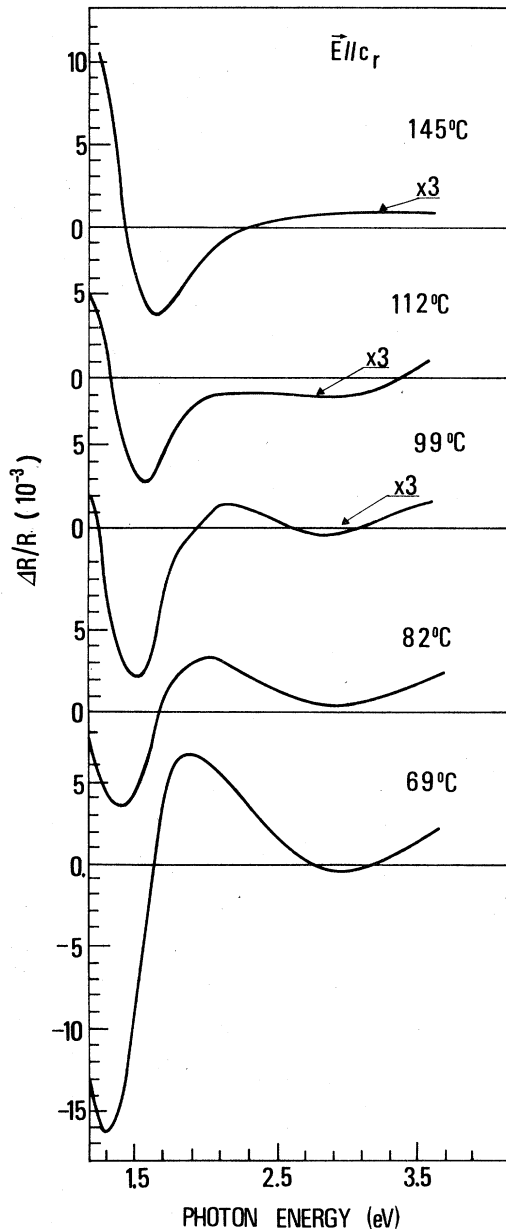


FIG. 2. Thermorefectance spectra of VO<sub>2</sub>, using polarized light  $\vec{E}||c_r$ , in the metal phase ( $T, T_c$ ) as a function of temperature, are plotted. The minimum at 1.6 eV, at higher temperature due to plasmon resonance, shows a red shift with decreasing temperature.

and  $\vec{E}||c_r$  spectra. The structure at 2.9 eV is not observed with the  $\vec{E}||c_r$  polarization.

In Fig. 3, the plasmon energy in metal VO<sub>2</sub> as a function of temperature, is plotted showing a large red shift approaching the transition temperature. In Fig. 4, the temperature-induced variation of  $\epsilon_1$  and  $\epsilon_2$  are plotted.  $\Delta\epsilon_1$  and  $\Delta\epsilon_2$  were calculated by Kramers-Kronig analysis of the thermorefectance spectra of high-temperature metal VO<sub>2</sub> using the dielectric constants of VO<sub>2</sub> are reported by Derbenwick.<sup>19</sup>

#### IV. DISCUSSION

##### A. Electronic structure of VO<sub>2</sub>

The band structure of metal rutile VO<sub>2</sub> has been calculated.<sup>16,20</sup> The results are in agreement with the molecular cluster calculations.<sup>21,22</sup> The V 3d derived states form two bands: one made up of two  $e_g$  states (energy width  $\sim 2$  eV) and the other made up of three  $t_{2g}$  states (energy width  $\sim 3$  eV) at lower energy. Only one electron per vanadium atom is in the  $t_{2g}$  narrow conduction band. The three  $t_{2g}$  molecular levels consist of two  $pd$  anti-

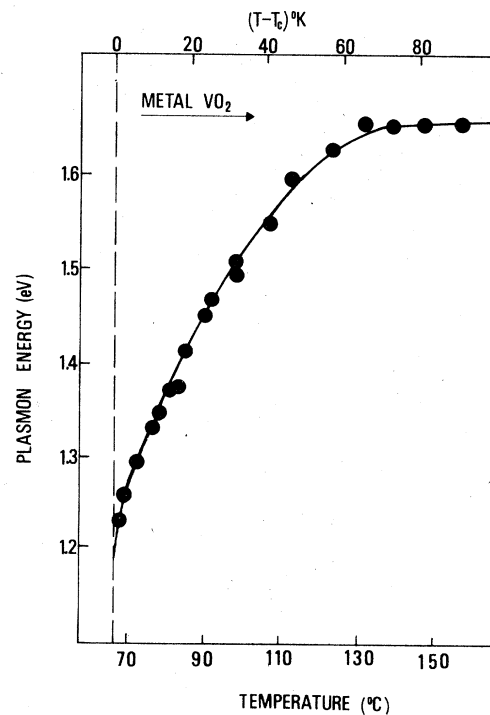


FIG. 3. Behavior of the plasmon energy  $\omega_p$  as a function of the crystal temperature.

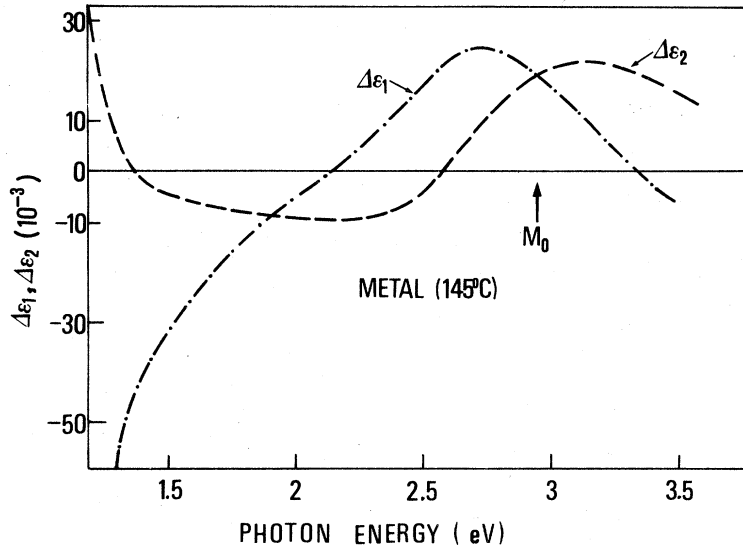


FIG. 4. Temperature-induced variations  $\epsilon_1$  and  $\epsilon_2$  of the real and imaginary parts of the dielectric constant. These values have been obtained by the Kramers-Kronig analysis of the thermoreflectance spectrum of metal  $\text{VO}_2$ .

bonding orbitals (the  $\pi^*$  band) and of one of overlapping V-V orbitals (the  $d_{||}$  band) parallel to the  $c_r$  axis. The Fermi level is crossing the  $d_{||}$  band overlapping the  $\pi^*$  band. The electronic interband transition at 2.9 eV is observed only for polarized light  $\vec{E} \perp c_r$ . Moreover, the Kramer-Kronig analysis shows a behavior of  $\Delta\epsilon_1$  and  $\Delta\epsilon_2$  (Fig. 4), typical of electronic transitions at  $M_0$  or  $M_3$  critical points if the band-energy shift or the broadening effects determine the reflectance modulation, respectively.<sup>23</sup> Disregarding broadening effects, this structure could be assigned to a transition from the top of a  $O_{2p}$  derived band to the  $\pi^*$  band at the Fermi level. In this case, the fact that this transition is practically unaffected by the MIT transition would indicate that the energy of the Fermi level is little affected by the MIT transition (Blaauw *et al.*<sup>6</sup>).

#### B. The plasmon in metal $\text{VO}_2$

The energy of a plasmon in a narrow partially filled conduction band is given by<sup>17</sup>

$$\omega_p^2 = \frac{4\pi N e^2}{\epsilon_\infty m^*} \left[ 1 - \frac{N}{N_0} \right] F \left[ \frac{N}{N_0} \right],$$

where  $m^*$  is an average effective mass at the Fermi energy  $E_F$ ,  $\epsilon_\infty$  is the background dielectric constant due to all interband transitions of energy higher

than  $\omega_p$ ,  $N$  is the actual electron density,  $N_0$  is its value for the completely filled band, and  $F$  is an unknown smooth function of the band filling alone (it is expected to be close to unity). In  $\text{VO}_2$  the conduction band is the  $t_{2g}$  band. The effective mass of electrons in the  $d_{||}$  band is much larger than that of the delocalized and hybridized  $\pi^*$  band. Assuming  $\epsilon_\infty = 5$  from the measure of optical constants<sup>19</sup> and the factor  $(1 - N/N_0) F(N/N_0) \simeq 1$ , we obtain  $m^* = 3.4m_0$ . The low value of the effective mass indicates that the electrons in the  $\pi^*$  band mainly contribute to the plasmon resonance, in fact, the effective mass of the localized  $d_{||}$  band has been estimated to be  $m^* = 60m_0$ .<sup>14</sup>

Using a simple two-band model a different interpretation of the plasmon frequency in  $\text{VO}_2$  can be given. The  $t_{2g}$  conduction band is assumed to be separated into the  $d_{||}$  band with an effective mass  $m^* = \infty$  and occupied by  $N_d$  electrons and an overlapping delocalized  $\pi^*$  band with effective mass  $m^* = m_0$  and occupied by  $N_\pi$  electrons. In this very simple model of  $\text{VO}_2$  the plasmon energy is given by

$$\omega_p^2 = \frac{4\pi N_\pi e^2}{\epsilon_\infty m_0}.$$

In the high-temperature metal phase  $\omega_p = 1.6$  eV and  $\epsilon_\infty = 5$ . Therefore, the density of delocalized electrons can be obtained  $N_\pi = 0.3$  electrons per vanadium atom. We also obtain the average

number of electrons trapped in the localized  $d_{||}$  band which do not participate in the plasmon resonance  $N_d = 0.7$  electrons per vanadium atom.

This result is in agreement with the electronic band-structure calculation<sup>20,16</sup> giving a large  $d$ - $d$  character (about 85%) of electronic states just above the Fermi level. As suggested by Zylbersztein and Mott,<sup>13</sup> assuming a  $(\pi^*)^{0.3}(d_{||})^{0.7}$  configuration at the Fermi energy of metal VO<sub>2</sub>, one can also account for both magnitude and temperature dependence of magnetic susceptibility.

We suggest that the electronic structure of metal VO<sub>2</sub> could be described by an interconfiguration-fluctuations (ICF) simple model where the system fluctuates between the  $(\pi^*)^1(d_{||})^0$  and the  $(\pi^*)^0(d_{||})^1$  configurations. This model can be used to extract from plasmon energy measurements, the partial occupation of the delocalized configuration, as is usually done in the experiments on rare-earth compounds which exhibit homogeneously mixed valence states.<sup>24</sup> In fact, the localized configuration of the system  $(\pi^*)^0(d_{||})^1$  does not contribute to the plasmon resonance. From the analysis of the plasmon energy in the high-temperature metal phase we have found an average partial occupation of 0.3 of the  $(\pi^*)^1(d_{||})^0$  delocalized configuration. It will be interesting to perform further experimental work to confirm the ICF model for VO<sub>2</sub>.

### C. Plasmon energy red shift at the metal-insulator transition

The theory of the plasmon energy shift due to the opening of a small band gap  $E_g$ ,  $E_g \ll \omega_p$ , predicts<sup>17</sup>

$$\omega_{ps}^2 = \omega_p^2 + \frac{1}{2} \{ E_g^2 - \omega_p^2 + [(E_g^2 + \omega_p^2)^2 - 4(1-f)E_g^2\omega_p^2]^{1/2} \},$$

where  $\omega_{ps}$  is the plasma frequency in the semiconducting phase,  $\omega_p$  is the plasma frequency in the metal phase, and  $f$  is the oscillator strength transfer, a quantity which varies from 0 to 1, determining how the plasmon is antiscreened by the electronic transitions following the opening of the band gap. Therefore we suspect that the plasmon energy in the semiconducting phase varies as a function of the actual value of  $f$  between

$$\omega_p^2 < \omega_{ps}^2 < \omega_p^2 + E_g^2.$$

The theory predicts no shift or a blue shift for  $\omega_p$ , in agreement with experiments on Ti<sub>2</sub>O<sub>3</sub> (Ref. 18)

and 2H-TaSe (Ref. 17), where the opening of the band gap  $E_g$  is due to crystal distortion<sup>11</sup> and to a charge-density-wave mechanism, respectively.

The plasmon energy in metal VO<sub>2</sub> shows a large red shift, as is shown in Fig. 3, beginning from 40 K above the transition temperature and decreasing with the decreasing temperature; finally, the plasmon vanishes in the semiconducting phase. This result is clearly in disagreement with the theory which takes into account only the opening of a small band gap.

This experimental result rules out the possibility that the driving mechanism of the MIT of VO<sub>2</sub> is a simple crystal distortion.<sup>2,15</sup> The average-effective-mass approximation can be used to explain the large red shift of the plasmon energy in metal VO<sub>2</sub> (as it approaches  $T_c$ ) by increasing the effective mass  $m^*$  from the value of  $3.4m_0$  at high temperature to  $5.6m_0$  at 69°C (only one degree above  $T_c$ ). Such a large increase of the effective mass (about 64%) in the metal phase (before the crystal structure distortion at  $T_c$ ) can only be due to a *large intraelectron correlation effect*. When the temperature approaches the transition temperature the local electron-electron interaction induces the localization of conduction electrons and this manifests itself as an increase of the effective mass. In the semiconducting phase, all the electrons are localized and the plasmon energy vanishes, due to the very large effective mass.

Using the two-band model, the red shift of plasmon energy is associated with an increase in the number of electrons trapped in the localized  $d_{||}$  band. In the high-temperature metal phase the valence configuration is  $(\pi^*)^{0.3}(d_{||})^{0.7}$  and becomes  $(\pi^*)^{0.18}(d_{||})^{0.82}$  at 69°C, only 1° above  $T_c$ . This model gives the increase of the number of localized electron trapped in the  $d_{||}$  band by electron correlation directly. In semiconducting phase all the electrons are expected to be localized. The plasmon vanishes giving the valence configuration  $(\pi^*)^0(d_{||})^1$  in agreement with band-structure calculations.

In the interconfiguration-fluctuation model for VO<sub>2</sub> the red shift of the plasmon resonance indicates an increase of the occupation probability of the  $(\pi^*)^0(d_{||})^1$  configuration with decreasing temperature from the high-temperature value of 0.7 to 0.82 at 1° above  $T_c$ . In the semiconducting phase the ICF's are frozen and all valence electrons are in the localized configuration.

Not only has a shift of the plasmon resonance been observed, but also a large temperature-dependent broadening of the resonance appears, increasing the temperature. This is consistent with a

strong temperature-dependent electron-phonon coupling in the metal phase, which reduces the plasmon lifetime. Further work is necessary for analysis if the plasmon screening from phonons is possible in VO<sub>2</sub>.

### V. CONCLUSION

The large red shift of the plasmon resonance in VO<sub>2</sub> gives direct evidence that the metal-insulator transition is a Mott-type transition from delocalized-to-localized electronic states. This is in

agreement with the large Hubbard intra-atomic electronic Coulomb interaction parameter  $U = 1.2$  eV calculated by Sommers and Doniach.<sup>14</sup>

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