ELECTRONIC AND LATTICE STRUCTURE OF CESIUM FILMS ADSORBED ON TUNGSTEN

A. U. MacRae, K. Müller,* J. J. Lander, J. Morrison, and J. C. Phillips
Bell Telephone Laboratories, Murray Hill, New Jersey 07974
(Received 24 March 1969)

Data on elastic diffraction and inelastic scattering of electrons by Cs adsorbed on W in monolayer lattices suggest that at monolayer densities equal to about half the bulk density the decay rate of surface plasmons is much greater than for similarly situated monolayers of approximately bulk density. The enhanced decay rate is interpreted as evidence for nonmetallic character of the low-density layer, as proposed by Wigner for a low-density gas and by Mott for low-density aggregates of odd-valence atoms.

A study of the interaction of cesium atoms with atomically clean surfaces of tungsten has revealed a system that has many of the properties associated with the metal-insulator (Mott) transition in crystalline arrays, discussed at length in a recent conference.[1] At the time of the conference, this transition had not been observed in crystalline arrays and indeed there was a question that it could ever be observed.[2] By means of low-energy electron diffraction (LEED) we have studied the structures of Cs deposited in vacuum on atomically clean W surfaces. The structures explain the minimum in work function observed previously.[3] At the minimum the outer layer of Cs corresponds to a low-density lattice structure with $r_s = 7.3$, where $\frac{4}{3}\pi(r_s a_0)^3$ is the volume per Cs atom, which is about 30% larger than the value of $r_s = 5.6$ for Cs metal. Inelastic energy losses suggest that the low-density outer layer is nonmetallic. It is possible that the primary cause for the nonmetallic character of the low-density layer is the Coulomb repulsion between electrons, which can create an insulating state, as discussed by Wigner[4] and by Mott.[5]

The apparatus used in this investigation was a three-grid display-type LEED system. Cesium was deposited on a clean (100) W surface, at background pressures in the low 10^{-10}-Torr range, by evaporation from a glass capsule. The crystal was cleaned by repeated heating in oxygen followed by heating at 10^{-10} Torr to remove the resultant oxide.[6] The surface cleanness was monitored by LEED and Auger-emission spectroscopy. The diffraction patterns were monitored concurrent with the adsorption by rotating the crystal in such a way that both the cesium and electron beams could strike the crystal.

LEED patterns were obtained with a primary-beam energy of about 30 eV, with the sample at room temperature. While adsorption on both (100) and (110) planes was studied, the low-density surface layer was studied on only the (100) plane.[7] For the (100) planes the first layer is observed to form a $c(2\times2)$ structure with a nearest-neighbor distance $d_1 = 4.46$ Å, considerably smaller than the bulk nearest-neighbor distance $d = 5.25$ Å. The density of this surface layer is $5\times10^{14}/\text{cm}^2$. The first layer also reduces the work function Φ by 2 eV, as shown in Fig. 1. Each Cs atom is therefore partially ionized, with one Cs^+ ion for two W atoms.

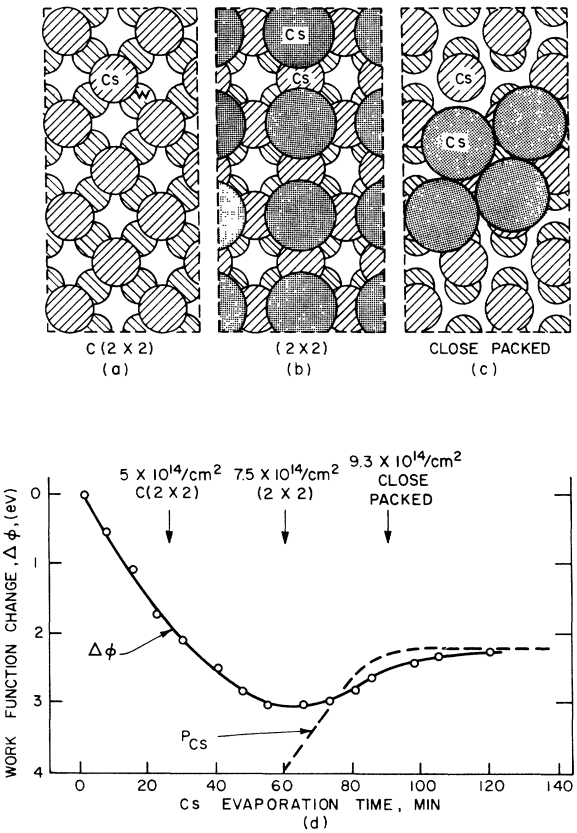

FIG. 1. Change of the work function Φ and the surface-plasmon intensity P_{Cs} as a function of Cs coverage on W (100) together with the associated surface structure. (a) The $c(2\times2)$ structure on W (100), (b) (2×2) on $c(2\times2)$, and (c) close-packed structure on $c(2\times2)$.

The second layer forms in two stages. The first stage is a $p(2\times2)$ structure that undergoes continuous rearrangement with the addition of further Cs atoms. The adsorption sites of the $p(2\times2)$ are assumed to be over "holes" in the underlying $c(2\times2)$ layer, so that the density of this layer is half that of the first layer, or $2.5\times10^{14}/\text{cm}^2$, and the nearest-neighbor spacing is 6.3 Å. The total coverage at this stage is $7.5\times10^{14}/\text{cm}^2$. The minimum in Φ coincides with the completion of the $p(2\times2)$ intermediate layer (see Fig. 1).

With addition of more Cs atoms, continuous rearrangement of the $p(2\times2)$ structure in the second layer takes place to form a close-packed hexagonal layer, with half the atoms remaining centered over "holes" in the first layer, while half are finally centered above points of contact of Cs ions in the first layer. The density of this layer is close to that of bulk Cs, with a nearest-neighbor spacing of 5.15 Å compared with the bulk value of 5.25 Å.

As this close-packed structure forms, the work function increases with its final value 0.3 eV higher than the value found at the minimum.

The origin of the minimum[3] in Φ at the completion of the low-density intermediate second layer can be explained in terms of the "smoothing" effect of Smoluchowski.[8] When a surface has hills and valleys of ionic potential [as for the $p(2\times2)$ structure, which is similar to the (110) faces of a sc crystal[8]], the kinetic energy of the electrons is reduced when charge flows from the hills to the valleys. In this way there arises a net positive dipole moment, which is eliminated when the second layer rearranges into the close-packed structure. Thus the minimum in Φ may be a geometrical effect. The slope $d\Phi/dN_S$ when the intermediate second layer is half-completed is associated with the smoothing effect and is about half that arising from the electronegativity difference between W and Cs.

Information on the electronic structure of the low-density intermediate layer is furnished by the secondary-emission spectrum with incident electron energies E_i of about 10 eV. An energy loss $\Delta E_i = 1.5$ eV is observed when the second layer has become completely close-packed and closely resembles bulk Cs. The intensity of this characteristic energy loss in inelastic scattering is reduced at lower Cs coverage and it disappears when the intermediate layer has just been formed (Fig. 1). Addition of more Cs (up to ten layers) beyond the close-packed layer leads to a shift of ΔE_i to 2.4 eV, as shown in Fig. 2.

It is assumed that the inelastic scattering is associated with the emission of surface plasmons defined[9] by $\text{Re}\epsilon(\omega) = -1$. In transmission through thick Cs films, bulk and surface plasmons have

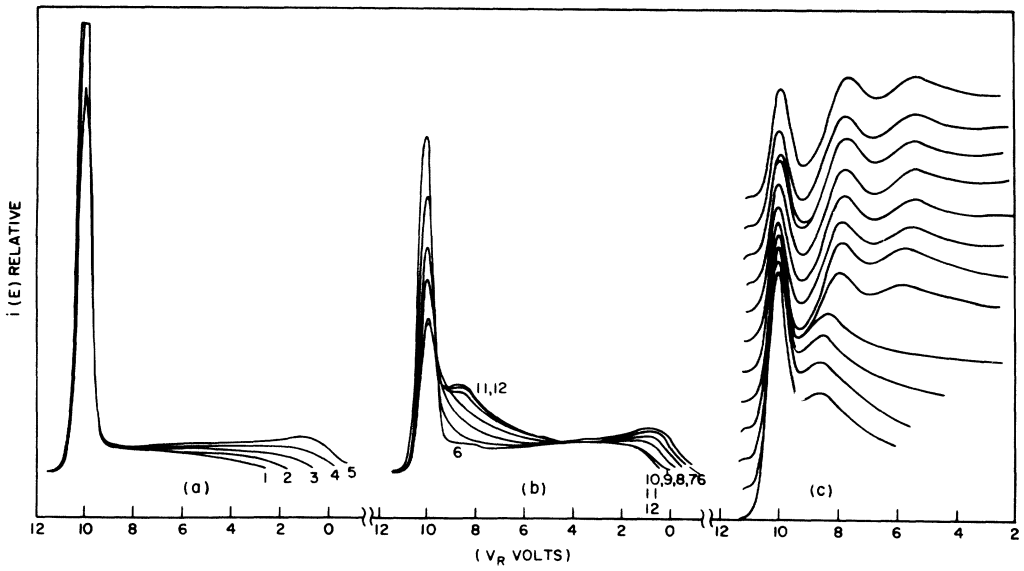

FIG. 2. Energy spectrum of backscattered electrons from a W (100) target as a function of Cs coverage for a 10-eV primary beam. The elastic component is seen at 10 eV and has a resolution (width at half-maximum) of about 0.5 eV. The cutoffs near zero energy are a measure of the change in surface work function. (a) Range from clean surface to minimum work function. (b) Range from minimum to saturation (for sample at room temperature). (c) Shift of the loss peak at 1.5 eV to about 2.4 eV with multilayer cesium deposition (produced by cooling the sample).

been identified[10] with respective energies 2.96 and 2.11 eV. For very thin films, however, the surface-plasmon mode[11] splits into two branches, ω_+ and ω_-, defined by

$$2\omega_{\pm}^{2} = \omega_p^{2}[1 \pm \exp(-ak_{\perp})], \quad (1)$$

where ω_p is the bulk plasma frequency, a is the film thickness, and $k_\perp$ the component of incident electron momentum normal to the film. Both branches of (1) have been observed in transmission-energy-loss experiments[12] through Al foils, and it is assumed here that the lower branch is contributing to the energy loss of backscattered electrons. Similar energy losses have been detected with Cs films on Ni,[13] and (1) accounts qualitatively for the dependence of ΔE_i on film thickness.

Several alternative loss mechanisms appear less likely. Interband scattering should scale roughly like r_s^{-2}; yet the difference in density of the close-packed second layer ($\Delta E = 1.5$ eV) and bulk Cs ($\Delta E = 2.1$-2.4 eV) is less than 10%. Either charge- or spin-density waves (CDW or SDW) of the type proposed by Overhauser[14] would produce additional diffraction spots, which are not observed. Because of the stabilizing effect of the first layer, this cannot be regarded as a decisive test of the validity of the Overhauser model of alkali metals at low densities.

For higher incident electron energies (~40 eV) both bulk and surface W plasmon losses of 25 and 16 eV, respectively, are observed. With Cs coverage an additional loss at 7.5 eV is observed which is believed to be associated with the W-Cs interface, where the first layer of Cs is bound so strongly to the W as to form an intermetallic compound. When the second layer is complete, however, it contributes very little to Φ, which indicates that it is essentially neutral, having been shielded from the W substrate by the first Cs layer. The intermediate second layer of Cs thus may be described as a low-density alkali-lattice monolayer. It appears from the disappearance of the surface-plasmon losses that the low-density second layer may not be in a normal metallic state. The intermediate layer contains 1 atom/unit cell, or if one insists (in spite of the different contributions to Φ) upon grouping the first and second layers together, there are 3 atoms/unit cell. In either case because of an odd number of electrons/unit cell there will be no energy gap between filled and empty states generated by the periodic potential.

We may suppose that because of the low density of the intermediate second layer it is in an insulating state with an energy gap E_g between the occupied states and the excited states which correspond to delocalization of at least one electron. From the fact that the LEED pattern changes continuously from the intermediate second-layer to the final second-layer structure it appears that this energy gap goes continuously to zero as the Cs density approaches the bulk value. The following rough calculation shows that E_g is small compared with $\hbar\omega_p$, but may be larger than $\Delta\Phi_2$ ~0.3 eV.

When an electron is removed from a localized atomic state to a distant region of the monolayer, the energy required is $\frac{1}{2}E_g$. This consists of two parts, an ionization energy W_I (estimated from the free-atom ionization energy) and a polarization energy E_p of the nearest neighbors. In the $p(2\times2)$ structure there are four neighbors at a distance $d = 6.32$ Å, and we assume an atomic volume $\Omega = d^3$. Neglecting dielectric dispersion we estimate that the polarization energy is given by

$$E_p = 4\frac{\Omega}{8\pi}(\epsilon_0 - 1)\left(\frac{e}{d^2}\right)^2, \quad (2)$$

where ϵ_0 is the static dielectric constant. We estimate (one-gap model) that

$$\epsilon_0 \sim (\hbar\omega_p/E_g)^2, \quad (3)$$

so that using (2) and (3) we can solve

$$\tfrac{1}{2}E_g = W_I - E_p \quad (4)$$

for E_g. One finds $E_g \sim 0.7$ eV.

Because E_g is larger than $\Delta\Phi_2$ we expect the presence of the first Cs layer to have little effect on the electronic structure of the second layer. Also E_g is smaller than $\hbar\omega_p$, so that even the Wigner-Mott state would be expected to exhibit bulk and surface plasmons. The apparent disappearance of the surface-plasmon losses may then be attributed to an enhancement of the decay rate (lifetime broadening) in the insulating state. Such an enhancement might arise because of the low-density insulating state. The exclusion principle would not inhibit the production of electron-hole pairs so effectively as it does in the usual case of a high-density electron gas.

In conclusion, it appears that the $p(2\times2)$ Cs surface layer discussed here represents an approximate experimental realization of an ideal electron gas with r_s about 7.3 (or slightly larger). It also appears that the metallic or nonmetallic character of such a layer can be identified

by inelastic scattering of low-energy electrons. Similar results (although corresponding to other r_s values) should be obtainable with any substrate plus nearly-free-electron metal film which exhibits a minimum in $\Phi(N_s)$.

We are grateful to Conyers Herring for pointing out the connection between this work and that of Smoluchowski, Ref. 8.

*Karlsruhe University, Karlsruhe, Germany.
[1]Proceedings of the International Conference on the Metal-Nonmetal Transition, San Francisco, Calif., March, 1968, Rev. Mod. Phys. 40, 673 (1968).
[2]J. F. Mott, Rev. Mod. Phys. 40, 677 (1968).
[3]J. B. Taylor and L. Langmuir, Phys. Rev. 44, 423 (1933).
[4]E. P. Wigner, Phys. Rev. 46, 1002 (1934).
[5]N. F. Mott, Proc. Phys. Soc. (London) 62, 416 (1969), and Phil. Mag. 6, 287 (1961).
[6]J. Anderson and W. E. Danforth, J. Frank. Inst. 279, 160 (1965).
[7]A. U. MacRae, K. Müller, J. J. Lander, and J. Morrison, to be published.
[8]R. Smoluchowski, Phys. Rev. 60, 661 (1941); C. Herring and M. H. Nichols, Rev. Mod. Phys. 21, 238 (1949).
[9]E. A. Stern and R. A. Ferrell, Phys. Rev. 120, 130 (1960).
[10]B. M. Hartley, Phys. Letters 24A, 396 (1967); C. Kung, Z. Physik 196, 311 (1966).
[11]R. H. Ritchie, Phys. Rev. 106, 874 (1957).
[12]A. Otto and J. B. Swann, Z. Physik 206, 277 (1967).
[13]T. A. Callcott and A. U. MacRae, Phys. Rev. (to be published).
[14]A. W. Overhauser, Phys. Rev. 167, 691 (1968).

PHONON-PUMPED NUCLEAR SPIN WAVES IN A FLOPPED ANTIFERROMAGNET*

A. Platzker and F. R. Morgenthaler
Department of Electrical Engineering, and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 4 April 1969)

Phonon-exchange pumping of nuclear magnon pairs in low-anisotropy flopped antiferromagnets is proposed and the effective threshold fields given. Although the electronic sublattice magnetizations are driven, magnetoelastically, far below their resonance frequency, the lower pump frequency compensates for the weakened dynamic coupling between nuclear and electronic magnons. The required phonon power density is thus low and well within experimental reach.

When a sufficiently intense elastic wave of the proper frequency propagates through an antiferromagnet, spin-wave pairs can be driven unstable because of coupling via the linear magnetostriction. This method of excitation – related to but different from photon exchange pumping[1] – is of special interest because the sign of the torque on each magnetic sublattice is opposite, giving rise to an "optical-like" excitation that brings the intersublattice coupling into play. Morgenthaler[2] has previously derived the thresholds for phonon parallel pumping of electronic magnon pairs in the unflopped state with special attention to $RbMnF_3$. Although the thresholds are predicted to be low, the pump frequency must be comparable with twice the electronic resonances frequencies – which for $RbMnF_3$ are typically in the 10-GHz range. Unfortunately, ultrasonic transducer fabrication in this range is not within the current state of the art; this fact has inhibited our experimental efforts to date. However, because the Mn^{55} ions carry a nuclear magnetic moment, the possibility exists of phonon pumping nuclear magnon pairs (or one nuclear and one electronic magnon) at a much lower frequency.

In this Letter we give the theoretical first-order instability thresholds for such processes in a flopped cubic antiferromagnet for the case of a longitudinal phonon propagating parallel to the equilibrium direction of the sublattice magnetizations. The threshold of purely electronic magnon pairs is included to allow comparisons. In all three cases the excitation is via the exchange interaction between the electronic sublattice magnetizations and the pumping is thus maximally efficient.[1] The threshold elastic powers required (roughly of the same order in the three situations) appear to be very low for antiferromagnets with weak anisotropy and reasonable magnon losses. The leading candidate appears to be $RbMnF_3$.

It has been shown by de Gennes et al.[3] that nuclear spin-wave branches exist due to the Suhl-Nakamura indirect interaction. The possibility of excitation of nuclear magnon pairs by parallel pumping with an rf field (photon parallel pumping) has also been considered by them but the

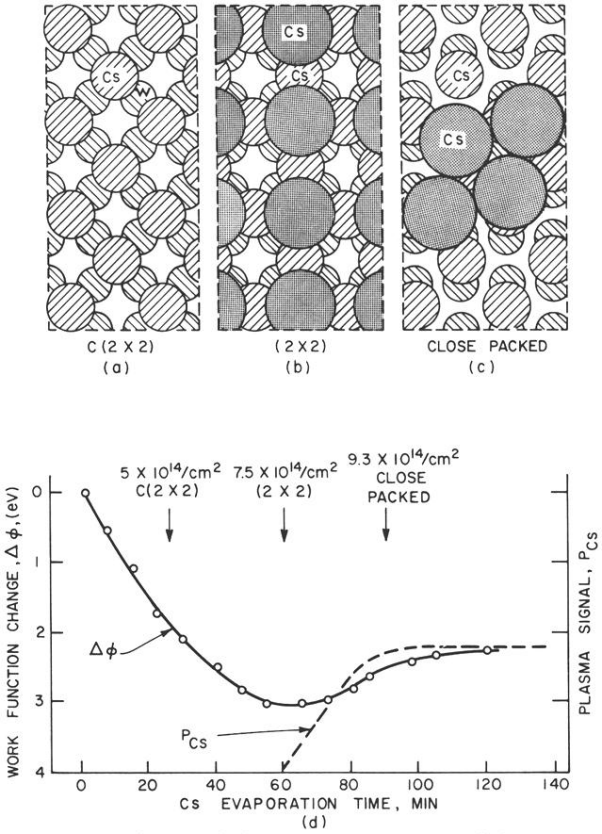

FIG. 1. Change of the work function Φ and the surface-plasmon intensity P_{Cs} as a function of Cs coverage on W (100) together with the associated surface structure. (a) The $c(2\times2)$ structure on W (100), (b) (2×2) on $c(2\times2)$, and (c) close-packed structure on $c(2\times2)$.