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Validity of Inelastic-Electron-Scattering Data in Determining the Metallic or Insulating Properties of Adsorbed Atomic Layers*

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It is pointed out that the observation of plasmon energy-loss peaks and determination of peak breadths in inelastic-electron-scattering experiments cannot be used to distinguish metallic or insulating materials. The recent claim, based on inelastic-electron-scattering data, by MacRae, Müller, Lander, Morrison, and Phillips that the initial (low-density) second layer of cesium adsorbed on a tungsten (100) surface is in an insulating state is considered not proved.

RESULTS have recently been published by MacRae, Müller, Lander, and Morrison[1] of a low-energy electron diffraction (LEED) study of cesium adsorbed on the (100) and (110) crystal surfaces of tungsten. These authors observed changes in the LEED pattern, the work function, and features of the secondary electron energy distribution as a function of the quantity of cesium evaporated onto the surface. The observation of an electron energy loss, identified as being due to surface plasmon excitation in Cs, was used as evidence by MacRae *et al.* to demonstrate the metallic character of the second Cs atomic layer found, in its final form, with an hcp structure on the W (100) surface. MacRae, Müller, Lander, Morrison, and Phillips[2] reported that the Cs surface-plasmon loss was not observed until the growth of the initial stage of the second layer was complete; from LEED measurements, the density of the initial stage of this layer was found to be about half the bulk value. The surface-plasmon loss peak was initially observed in broadened form and became sharper with increasing Cs coverage. These observations were used by MacRae *et al.*[2] as evidence for the initial stage of the second layer being in an insulating state and it was suggested that a crystalline system had been found with a metal-insulator (Mott) transition.[3]

In view of the importance of this conclusion and the fact that similar observational criteria might be used in future work, we wish to question some of the assumptions and conclusions in the analyses of MacRae *et al.*[1,2] Specifically, we wish to show that the observation of plasmon energy losses and a measure of the breadths of the loss peaks cannot be used as adequate tests for metallic properties (as defined by the existence of an unfilled Brillouin zone and relatively high electrical conductivity).

Volume plasmon excitations in an infinite[4] medium usually[5] occur at frequencies such that the complex wave-number and frequency-dependent dielectric constant $\epsilon(k,\omega)$ is small compared to unity. At the optical frequencies corresponding to the usual energy losses of at least a few eV, the optical conductivity [defined by $\sigma=\omega\epsilon_2(0,\omega)/4\pi$, where $\epsilon=\epsilon_1+i\epsilon_2$] is considerably different from the dc conductivity. For example, materials such as Be, Ge, Bi, and Al_2O_3, which have dissimilar electronic characteristics and considerably different electrical conductivities at low frequencies, have roughly comparable values of $\sigma(\omega)$ for photon energies between 10 and 25 eV and a dominant energy loss in this range that can be associated with volume plasmon excitation.[5a] On the other hand, copper has a high conductivity at low frequencies but does not have a well-defined volume-plasmon energy loss.[5,6] Similar remarks can be made concerning surface-plasmon energy losses, and we conclude that inelastic scattering attributed to plasmon excitation is not exclusively a metallic characteristic and that metals do not always have plasmon energy losses.

MacRae *et al.*[2] state that the first, partially ionic layer of Cs is bound so strongly to the W as to form an intermetallic compound. The deposition of the second layer of Cs leads to a relatively small change in work function and this layer was considered to be "essentially neutral." MacRae *et al.* describe the latter layer as a low-density alkali-lattice monolayer and then implicitly assume in their analysis that the layer is isolated electronically from the substrate; such an

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[1] A. U. MacRae, K. Müller, J. J. Lander, and J. Morrison, Surface Sci. **15**, 483 (1969); see also J. J. Lander and J. Morrison, *ibid.* **14**, 465 (1969).

[2] A. U. MacRae, K. Müller, J. J. Lander, J. Morrison, and J. C. Phillips, Phys. Rev. Letters **22**, 1048 (1969).

[3] The metal-insulator transition proposed and discussed by N. F. Mott [Rev. Mod. Phys. **40**, 677 (1968), and earlier papers cited therein] may occur with change in atomic spacing. Mott summarizes reasons to believe that it may be very difficult in principle to identify such a transition in a crystalline lattice. In practice, the transition may be difficult to identify an account of lattice distortion; as Mott points out, a change in crystal structure may lead to a band gap. It therefore seems inappropriate that the results of MacRae *et al.* (Ref. 2), associated with changes in surface structure, should be interpreted in terms of a Mott transition.

[4] The "infinite" solid is assumed to have dimensions d much greater than $d=\hbar v/\Delta E$ where v is the incident electron velocity and ΔE is the energy loss under consideration. For 30-eV incident electrons and $\Delta E=2$ eV [conditions approximating those in the experiments of MacRae *et al.* (Refs. 1 and 2)], $d=11$ Å.

[5] C. J. Powell, J. Opt. Soc. Am. **59**, 738 (1969).

[5a] L. Marton and J. Toots, Phys. Rev. **160**, 602 (1967); J. Toots, H. A. Fowler, and L. Marton, *ibid.* **172**, 670 (1968); J. Toots and L. Marton, J. Opt. Soc. Am. **59**, 1305 (1969); E. T. Arakawa and M. W. Williams, J. Phys. Chem. Solids **29**, 735 (1968).

[6] B. R. Cooper, H. Ehrenreich, and H. R. Philipp, Phys. Rev. **138**, A494 (1965).

assumption seems extremely unreasonable. The existence of an insulating state in the low-density second layer was postulated by MacRae *et al.*[2] who then attempted to indicate the plausibility of this assumption. An energy-band gap E_g was estimated from the difference between two relatively large and nearly equal quantities, a free-atom ionization energy and a polarization energy which was estimated with the use of a formula due to Penn.[7] This formula was derived with a parameter E_g representing an "average" energy gap for an infinite solid and its application to a two-dimensional atomic layer (with or without a substrate) has not been justified.[8]

MacRae *et al.*[2] mention that the proposed insulating state would be expected to exhibit bulk and surface plasmons. They remark that 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," and that "such an enhancement might arise because of the low-density insulating state." The authors suggest that the damping rate is greater in the "low-density" state although it seems unlikely that the stated density variation alone would lead to an appreciable change in the peak breadths, especially when it is recalled that the electron density in the layer should not be computed as if the layer was physically isolated from the substrate.[9] In any case, the valence electron densities of normal conductors and insulators are of comparable magnitude, as are the breadths of the surface- and volume-plasmon peaks in Be, Ge, Bi, and Al_2O_3. That is, the breadth of a plasmon loss peak is not a valid indication of whether the material is metallic or nonmetallic.

It is possible that the extra surface-plasmon peak broadening with decreasing film thickness could be due to geometrical restrictions on the available range of plasmon wavelengths. Such extra broadening in the Al volume-plasmon loss peak has been observed as a function of decreasing crystallite grain size[10] but, even if a thickness-independent macroscopic $\epsilon(k,\omega)$ was assumed, the available formulas[11] could not be used for valid calculations in the thickness range of present interest.[12] Alternatively, the damping rate of the surface plasmons in thin Cs layers could be enhanced by the presence of the substrate; the value of $\epsilon_2(0,\omega)$ for W is about 20 for $\hbar\omega = 2$ eV.[13]

MacRae *et al.*[2] briefly consider and then dismiss energy-loss mechanisms other than plasmon scattering. In their argument, they overlook the fact that the damping or nonexistence of plasmon losses indicates the existence of significant interband-electronic transitions (by the f sum rule). Inspection of Fig. 2 of Ref. 2 shows that the ratio of intensities due to inelastic and elastic electron scattering increases with Cs coverage, as expected. Further calculations of the thickness-dependent dielectric properties of the adsorbed Cs layers would be required to interpret the energy-loss data of MacRae *et al.*[2]

It is concluded that observation of plasmon energy-loss peaks and determinations of peak widths cannot be used to distinguish metallic or insulating materials. The claim by MacRae *et al.*[2] that the initial second layer in the adsorption of Cs on W (100) is in an insulating state is regarded as not proved.

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[7] D. R. Penn, Phys. Rev. **128**, 2093 (1962). See also G. Srinivasan [*ibid.* **178**, 1244 (1969)] and J. L. Fry [*ibid.* **179**, 892 (1969)] for comments on Penn's model.

[8] It should also be remarked that though Penn's formula (Ref. 7) yields a value of E_g for an infinite solid that is in moderate agreement with the photon energy at which the optical absorption is a maximum (e.g., for Ge and Si), the value of E_g is considerably greater than the energy separation between the valence and conduction bands (e.g., by a factor of ~5 for Ge).

[9] J. W. Gadzuk, Phys. Rev. **B1**, 1267 (1970).

[10] C. Kunz, Z. Physik **167**, 53 (1962); C. v. Festenberg, *ibid.* **207**, 47 (1967).

[11] R. H. Ritchie, Phys. Rev. **106**, 874 (1957); E. A. Stern and R. A. Ferrell, *ibid.* **120**, 130 (1960); T. Kloos, Z. Physik **208**, 77 (1968).

[12] R. H. Ritchie and R. E. Wilems, Phys. Rev. **178**, 372 (1969). See also: K. L. Ngai, E. N. Economov, and M. H. Cohen, Phys. Rev. Letters **24**, 61 (1970).

[13] S. Roberts, Phys. Rev. **114**, 104 (1959).