Electron Self-Energy in a Metal Measured from a Beam-Threshold Effect in Low-Energy Electron Diffraction

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(Received 1 October 1982)

Low-energy electron diffraction from the copper (111) surface contains fine structure which is correlated with the emergence of beams in the metal. It is found that the fine structure determines points on the inner potential versus energy curve with virtually no dependence on surface relaxation. Postulating that the absorption of electrons is relatively weak in the ion cores, the authors present a low-energy electron-diffraction theory which predicts that electrons can channel through the ion cores of the layers parallel to the surface.

PACS numbers: 61.14.Hg, 68.20.+t

It seems that today's accuracy of all kinds of spectroscopy involving electron diffraction is limited, on a fundamental level, by the uncertainty in the determination of the inner potential.[1] The great problem is that the electron exchange-correlation self-energy, which makes an essential contribution to the inner potential, varies significantly with the energy of the scattered electron.[2] Desirable for an improvement of the electron-diffraction methods would be to find an inner potential from evidence independent of surface structure.

In this Letter we report a low-energy electron-diffraction (LEED) observation that the 00 spectrum from the copper (111) surface contains fine structure correlated with the threshold for emergence of new beams inside the metal.[3] We shall call such a threshold a "subthreshold" and the accompanying fine structure the "subthreshold effect." Consider a beam of surface wave vector $\vec{k}_{xy}+\vec{g}$, where $\vec{k}_{xy}$ is the surface component of the wave vector of the incident electron and $\vec{g}$ is a unit-cell vector in the reciprocal surface net. At the energy of incidence E the beam $\vec{g}$ propagates in the z direction in the metal (the metal occupies the half-space $z>0$) with the wave-vector component k_{gz} and the energy contribution E_{gz},

$$k_{gz}=(E_{gz}-i\beta)^{1/2}, \quad E_{gz}=E-V_0-|\vec{k}_{xy}+\vec{g}|^2, \qquad (1)$$

where V_0 is the inner potential and β is a phenomenological absorptive potential. The subthreshold of beam $\vec{g}$ is the energy E where $E_{gz}=0$. It has to be distinguished from the threshold $E_{gz}+V_0=0$, where the beam $\vec{g}$ emerges into the vacuum. The latter threshold is the upper energy limit of a Rydberg-type LEED spectrum associated with metastable electron states at the vacuum-metal interface.[4] Regarding the subthreshold effect we argue that it is caused by an anisotropy of the electron absorption in the bulk.

We obtain a one-parameter model for the anisotropy by assuming that the electron absorption is different in the ion cores and in the interstitial region. The model is supported by LEED calculations which comprise an anisotropic electron absorption and which accurately agree with the observed fine structures. We find that the subthreshold effects associated with different beams permit an accurate determination of the inner potential $V_0(E)$ corresponding to the energy-dependent self-energy of the LEED electron. An important novelty of the method is that $V_0(E)$ is obtained with virtually no dependence on surface relaxation in the case of a clean metal.

Figure 1 shows the sample-to-ground current together with the 00 spectrum of LEED on copper (111) in the energy range 15–30 eV. One sees a Bragg peak of 10% intensity at 22.5 eV and, leaning on that, a shoulder of 5% intensity at 19.5 eV. The shoulder is extremely sensitive to sample tilts and is observed only within 2° from the surface normal. Figure 2 shows the 00 spectrum recorded in the energy range 30–190 eV with the incident beam tilted 5° away from the surface normal towards [10] in the reciprocal surface net. Three subthreshold effects are clearly visible in the 00 spectrum: the shoulder at 19.5 eV, the sharp peak at 73.6 eV, and the peaklet at 109 eV. These fine structures are correlated with the internal emergence of the following beams: the

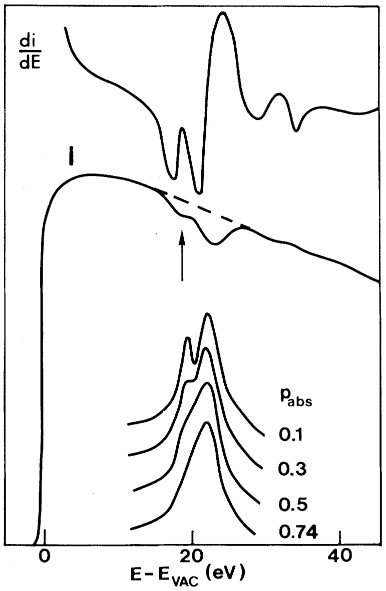

FIG. 1. LEED from Cu(111). Sample-to-ground current, experiment (at the top); 00 spectrum, theory (at the bottom). The arrow indicates a subthreshold effect at 19.5 eV.

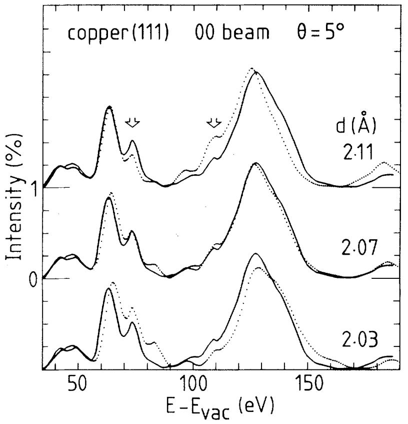

FIG. 2. LEED from Cu(111). Experiment, solid line; theory, dotted line; d, top-layer spacing. Arrows indicate strong subthreshold effects at 73.6 and 109 eV.

triplets symmetric to 10 and 01, the mirror doublet $\bar{2}1, \bar{1}\bar{1}$, and the mirror doublet $\bar{2}2, 0\bar{2}$. Another three subthreshold effects are barely discernable as slope variations at 83, 100, and 136 eV. These fine structures are correlated with the internal emergence of the following beams: the mirror doublet $\bar{1}2, 1\bar{2}$, the mirror doublet $11, 2\bar{1}$ together with the singlet $\bar{2}0$, and the singlet 20. In a LEED experiment on copper (111) Bedell and Farnsworth[3] observed the subthreshold effect near 18.3 and 77.5 eV at normal incidence, referring to it as a "resonance"; also, on nickel (111), a subthreshold effect was seen.

To explain the subthreshold effect we consider a new model for the interlayer attenuation in LEED. The customary LEED theory[5] uses a jellium picture for describing the propagation of beams in the stack of layers parallel to the surface. In that picture a beam $\vec{g}$ is a plane wave $\exp(i\,\mathrm{Re}k_{gz}z)$ times an attenuation function $\exp(-\mathrm{Im}k_{gz}z)$. We shall now generalize the jellium picture for the interlayer attenuation by allowing for different electron absorption in the ion cores and in the interstitial region. We conceive a simplified model for the electron absorption where the ion cores are rolled out to a homogeneous plate of absorbing ionic material. If the thickness of the layer is d and the packing fraction of the ion cores is p (touching spheres in a fcc lattice have $p = 0.74$), the ionic and the interstitial plate have thicknesses pd and $(1-p)d$. We take the attenuation to be $\exp[-\mathrm{Im}k_{gz}(1-p)d]$ across the interstitial plate and $\exp(-\mathrm{Im}k_{gz}p_{\mathrm{abs}}d)$ across the ionic plate, where p_{abs} is a new parameter. The attenuation is thus parametrized, for a given energy E, in terms of β in the interstitial plate and in terms of β and p_{abs} in the ionic plate. The present model implies that the interlayer propagator P_g of beam $\vec{g}$ attenuates as

$$|P_g| = \exp[-\mathrm{Im}k_{gz}(1-p+p_{\mathrm{abs}})d]. \tag{2}$$

The significance of the new approximation for $|P_g|$ is understood after normalization of $|P_0|$ to $\exp(-a_0 d)$, where a_0 is the attenuation exponent of the transmitted 00 beam. The propagating beams ($E_{gz} > |\beta|$) are practically independent of p_{abs}, while the internally emergent beams ($E_{gz} = 0$) have the attenuation exponent $a_0^{1/2}E_{0z}^{1/4}(1-p+p_{\mathrm{abs}})^{1/2}$. When $p_{\mathrm{abs}} < p$, the amplitude of the internally emergent beams is enhanced in comparison with customary LEED theory,[5] where $p_{\mathrm{abs}} = p$.

A small value of p_{abs} opens a transparent scattering channel $\vec{g}$ directed a few degrees off the surface. The flux in the channel scatters back into the specular beam, and if all contributions coming from different layers are in phase, a fine structure appears in the 00 spectrum. Under such conditions the wave field of channel $\vec{g}$ has the wave vector $\mathrm{Re}k_{gz} = (|\beta|/2)^{1/2}$ (for $E_{gz} = 0$) and the attenuation exponent a_0 (the same as for the 00 beam). Applying the Breit-Wigner formula to this attenuated state, one finds that the subthreshold effect has the peak width $\Delta E = (8|\beta|)^{1/2}a_0$. Typically ΔE is 2 eV for $\beta = -4.5$ eV and $a_0 = 0.1$ a.u.

The interlayer attenuation of expression (2) is now used in a LEED calculation on copper (111), while the ion-core scattering potential is designed in the muffin-tin fashion. We take the Hartree part of the potential from a ground-state band-structure calculation[6] and, using the electron density associated with that band structure, we calculate an excited-state exchange-correlation self-energy[7] by means of the local-density theory of Hedin and Lundqvist.[2] The resulting inner potential is drawn in Fig. 3. The calculated LEED spectra in Figs. 1 and 2 exhibit subthreshold effects which agree excellently with the measured ones, provided $p_{\rm abs}$ is set around 0.4 (cf. $p=0.74$) and the precalculated inner potential is shifted properly. A decrease of $p_{\rm abs}$ strengthens the intensity modulations of the subthreshold effects, while their positions are left unchanged like the rest of the spectrum. The inner potential determined from the experiment is plotted in Fig. 3.

The principal evidence speaking in favor of the mechanism of electron channeling is that the fine structure has the width 2 eV in both theory and experiment (cf., in particular, 19.5 eV in Fig. 1 and 109 eV in Fig. 2). The internally emergent beams have almost no spillout in the vacuum; therefore the narrowness of the fine structure definitely points at wave coherence down to the full penetration depth of LEED in the metal. Moreover, Fig. 2 shows that the calculated subthreshold effects stay in fixed positions when the top-layer displacement is varied, in contradistinction to the major Bragg peaks at 52 and 128 eV which move considerably. The empirical result that $p_{\rm abs}$ is smaller than p for copper (111) in the energy range 19–109 eV indicates that the LEED electron interacts weakly with plasmons inside the ion cores and is likely to channel within an atomic layer. This kind of channeling is complementary to that prevailing in 100-keV electron microscopy,[8] where the electrons channel between the rows of atoms because of ample atomic excitation at 100 keV.

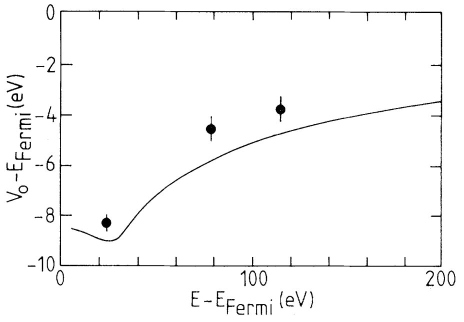

FIG. 3. Inner potential of Cu vs electron energy. Curve, theory; points, experiment.

In a LEED analysis the crystal surface is mimicked by a model involving a set of structural parameters. The best choice of parameters is found by minimization of reliability indexes[9] or metric distances,[10] defined in such a way as to emphasize any misfit between Bragg-type structure in the LEED spectra. At the present status of LEED the inner potential $V_0(E)$ is included in the minimization procedure just as another structural parameter by means of the approximation

$$V_0(E)=V_0^{\rm trial}(E)+\Delta V_0, \tag{3}$$

where $V_0^{\rm trial}(E)$, fixed, is a plausible choice of inner potential and ΔV_0, adjustable, is a shift that is constant in the energy range under consideration. In the literature one recognizes three types of $V_0^{\rm trial}(E)$: (i) a constant value,[11] (ii) a curve ensuing from fits of Bragg structure in short energy intervals,[12] and (iii) a function of energy precalculated from electron-gas theory.[7] In a curve fitting to major Bragg peaks, ΔV_0 is strongly correlated with surface relaxation. A great promise for LEED is that the inner potential and the surface relaxation can be determined separately, if the one quantity is extracted from subthreshold effects and the other is found from Bragg structures. The accuracy of a $V_0(E)$ determined from a subthreshold effect is of the order of 0.1 eV, if the energy scale is fixed by means of the Rydberg spectrum of the corresponding vacuum threshold.

In summary, we report that LEED from the copper (111) surface contains fine structure which is correlated with the emergence of beams in the metal. We interpret the fine structure as due to channeling of electrons through the ion cores of the layers parallel to the surface. Each fine structure fixes a point on the curve of inner potential versus energy, $V_0(E)$. The suggestions of this Letter are, with respect to theory, that the exchange-correlation self-energy calculated for the electron gas can be checked against a measured $V_0(E)$ for the material under consideration, and, with respect to applications, that all electron spectroscopy of surface materials can be interpreted in terms of a very accurate wave-number standard $[E-V_0(E)]^{1/2}$.

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[1] J. B. Pendry, in *Electron Diffraction 1927–1977*,

edited by P. J. Dobson, J. B. Pendry, and C. J. Humphreys, IOP Conference Series No. 41 (Institute of Physics, Bristol, 1978), pp. 205–217.

[2] L. Hedin and B. I. Lundqvist, J. Phys. C 4, 2064 (1971).

[3] L. R. Bedell and H. E. Farnsworth, Surf. Sci. 41, 165 (1974).

[4] J. Rundgren and G. Malmström, Phys. Rev. Lett. 38, 836 (1977).

[5] J. B. Pendry, *Low Energy Electron Diffraction* (Academic, London, 1974).

[6] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[7] J. Neve, J. Rundgren, and P. Westrin, J. Phys. C 15, 4391 (1982).

[8] J. M. Cowley, *Diffraction Physics* (North-Holland, Amsterdam, 1981).

[9] E. Zanazzi and F. Jona, Surf. Sci. 62, 61 (1977); J. B. Pendry, J. Phys. C 13, 937 (1980).

[10] J. Philip and J. Rundgren, in *Proceedings of the Conference on Determination of Surface Structure by LEED*, edited by P. M. Marcus (Plenum, New York, 1982), p. 16.

[11] D. L. Adams, H. B. Nielsen, and M. A. van Hove, Phys. Rev. B 20, 4789 (1979).

[12] Y. Gauthier, R. Baudoing, and L. Clarke, J. Phys. C 15, 3231 (1982).

New Phenomenon of the Molecular Liquid State: Interaction of Molecular Rotation and Translation

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(Received 2 November 1982)

The technique of computer simulation is used to reveal a new and unsuspected phenomenon of the molecular liquid state which is observable by several different spectroscopic techniques. The phenomenon is explained in terms of the effect of a molecule's rotation on its own translation (or vice versa). This is directly measurable in optically active molecules, and exists for all molecules in the liquid state.

PACS numbers: 61.25.Em

The technique of computer simulation has been developed to the point where the molecular dynamics of optically active molecules in the liquid state can be studied in detail for the first time. These molecules have no center of inversion and exist as C_s mirror-image pairs, known as enantiomers. An equimolar mixture of these enantiomers is a racemic mixture.

In this Letter I report the first computer simulation of two enantiomer liquids and of their 50/50 racemic mixture. A new, unexpected, and generally valid spectroscopic phenomenon is revealed by these computations, and can be explained precisely in terms of rotation/translation coupling on a fundamental, molecular scale.

The algorithm was based on a listing from Collaborative Computational Project 5 (CCP5) of the Science and Engineering Research Council (U.K.), extensively modified by Ferrario *et al.*[1-5] The *R* and *S* enantiomers of 1,1-chlorofluoroethane (Fig. 1) were modeled with a 5×5 site-site potential consisting of atom-atom Lennard-Jones terms and partial charges located at the atomic sites. The Lennard-Jones parameters were

$$(\epsilon/k)(\mathrm{Cl\text{-}Cl}) = 127.9\ \mathrm{K};\ \sigma(\mathrm{Cl\text{-}Cl}) = 3.6\ \text{Å}; \quad (1)$$

$$(\epsilon/k)(\mathrm{C\text{-}C}) = 35.8\ \mathrm{K};\ \sigma(\mathrm{C\text{-}C}) = 3.4\ \text{Å}; \quad (2)$$

$$(\epsilon/k)(\mathrm{H\text{-}H}) = 10.0\ \mathrm{K};\ \sigma(\mathrm{H\text{-}H}) = 2.8\ \text{Å}; \quad (3)$$

$$(\epsilon/k)(\mathrm{F\text{-}F}) = 54.9\ \mathrm{K};\ \sigma(\mathrm{F\text{-}F}) = 2.7\ \text{Å}; \quad (4)$$

$$(\epsilon/k)(\mathrm{CH_3\text{-}CH_3}) = 158.6\ \mathrm{K};\ \sigma(\mathrm{CH_3\text{-}CH_3}) = 3.5\ \text{Å}. \quad (5)$$

Partial charges were used as given by Nafie, Polavarapu, and Diem.[6]

At 293 K, with an estimated liquid density of 1.1 g mol^{-1}, 108 molecules of each enantiomer were used in two separate molecular-dynamics runs. Data from these runs were used to evaluate a wide range of time correlation functions in both the laboratory and rotating frames of reference,[7] the latter defined for convenience as that of the principal molecular moments of inertia.