In our calculation we have neglected any pressure dependence of $n_c(T)$ and the possibility of an interphase surface tension. The measured pressure variation of $n_c(T)$ at positive pressures,[20] however, suggests that these effects would tend to cancel each other. More serious objections to this semiphenomenological approach can certainly be raised. We have employed continuum mechanics and used properties of bulk He^3-He^4 solutions in attempting to explain a phenomenon which is probably localized only over a few angstroms about the vortex core center. Such an approach is questionable when one considers that the thermal de Broglie wavelength of a He^3 atom is on the order of 15–20 Å. However, the data presented here, as well as the indirect evidence discussed earlier, indicate that the basic notion of He^3 condensation onto vortices is correct, and it seems quite unlikely that the good agreement between our data and the calculation is entirely fortuitous.

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Anisotropic Interband Effects in Electroreflectance of Ag†

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Measurements of the normal-incidence electroreflectance of clean, strain-free single crystals of Ag and Au with use of a novel drop-electrolyte technique shown an anisotropy on the (110) face of Ag which is not present on Au. It can be explained by field-induced indirect interband transitions which are observed in Ag but not in Au. This work shows that part of the electroreflectance spectrum of Ag arises from electrons which interact with the periodic crystal potential.

The intense electric field ($\lesssim 10^7$ V/cm), which can be induced in the interface region between a concentrated (1 M) electrolyte and a metal, penetrates less than one atomic layer into the metal (Thomas-Fermi screening length $\lesssim 0.8$ Å) and only a few atomic radii into the electrolyte (Debye length $\lesssim 0.3$ Å). A change in the electric field can produce a change in the optical reflectivity

of the metal-electrolyte system.[1-10] This technique, metallic electroreflectance, is a sensitive probe of the electron energy structure of the interface region and can provide stimulation input toward current efforts to understand solid surfaces.

McIntyre[8] has established that the metal surface provides the major contribution to the electroreflectance signal, and together with Aspnes[11] has proposed the most successful of the several theories[3,6,7] concerning the mechanism. They assume that bound electron states are unaffected by an applied field and that only the plasma frequency of the free-electron gas in the interface region is shifted. More recently, Bower[12] has proposed an explanation of the observed anisotropy in oblique-incidence metallic electroreflectance which depends on the contribution of bound electrons. In this Letter we present the results of the first electric-field-modulation measurements on properly prepared single-crystal metal surfaces using polarized light at *normal incidence*. We observe a marked anisotropy in the normalized reflectivity change $(\Delta R/R)$ of silver near 3.9 eV which cannot be explained by existing theories that do not allow for crystal-structure effects. As we will show, the results of our experiment can be explained by symmetry arguments that implicate the participation of interband effects in metallic electroreflectance.

We used a novel technique, similar to one employed in electrochemical studies by Dickertmann, Schultze, and Velter,[13] which eliminates the danger of straining the sample and reduces the effect of impurities. The solution was restricted to a drop (volume $\lesssim 0.1$ ml) which rested on the oriented horizontal surface of the otherwise unrestrained single-crystal sample. The top of the drop was flattened by a small disk of optical quartz which was supported from the side by a quartz rod. Electrical contact with the drop was achieved through two solution-bearing, diffusion-blocked, glass capillaries leading to electrode compartments. Modulation of the surface electric field was achieved through changes in the electric potential which was applied by a platinum wire in one compartment and measured with respect to a saturated calomel reference electrode (SCE) in the second compartment. A syringe system was included to renew the electrolyte in the drop. The whole assembly was placed in a closed atmosphere of purified nitrogen (passed through activated charcoal and over hot copper turnings) to exclude the interference of

oxygen and other airborne contamination. The $1M$ electrolyte was prepared from reagent-grade KOH using twice-distilled water produced from alkaline permanganate solution in a closed quartz still. All glass and Teflon parts which contacted the solution were cleaned in hot sulfuric acid, then flushed with twice-distilled water until no trace of the hydrogen ion was found in the rinse. The silver crystal (99.99% pure) was oriented, spark cut, and mechanically polished through 0.3 μm alumina to produce a flat surface. The plastically deformed layer was then removed by potential-controlled electropolishing[14] in a conventional electrochemical system. Chemical reduction of any contaminating surface film was performed *in situ* after the drop configuration was established. This was achieved by maintaining conditions for the evolution of atomic hydrogen by electrolysis at the silver surface for 30 min, after which the drop electrolyte was renewed. A 1000-Hz sinusoidal potential variation of 0.1 V peak-to-peak (relative to the SCE) was superimposed on a feedback-controlled bias potential. The metal-electrolyte interface differential capacitance, which is very sensitive to surface active contamination, was extracted from our observed charging current. The variation of capacitance with bias potential shows no hysteresis and has the same shape, and nearly the same magnitude, as the differential capacitance of the Ag–$1M$-KOH interface recorded with extreme precautions by Zelinski, Bek, and Maslii.[15]

The sample was illuminated by monochromatic (0.02 eV resolution) plane polarized light in a cone which struck the surface with a range of incident angles between 0° and 5°. The reflected light was directed to a photomultiplier detector whose dc signal was held constant with a gain-servo system. A lock-in amplifier was used to separate the ac signal (proportional to $\Delta R/R$) which was in phase with the applied potential modulation.

Figure 1 shows our electroreflectance results on the (110) and (100) surfaces of silver. The modulating field direction $(\hat{F})$ was perpendicular to the sample surface, while the light polarization direction $(\hat{e})$ was always parallel to that surface. With the field parallel to the [100] crystal axis (curve a) the dominant negative peak at 3.91 eV was polarization independent. When the field was oriented parallel to the [110] axis (curves b and c) this structure appeared at 3.87 eV and displayed a polarization dependence which was correlated to the two-fold symmetry about this axis.
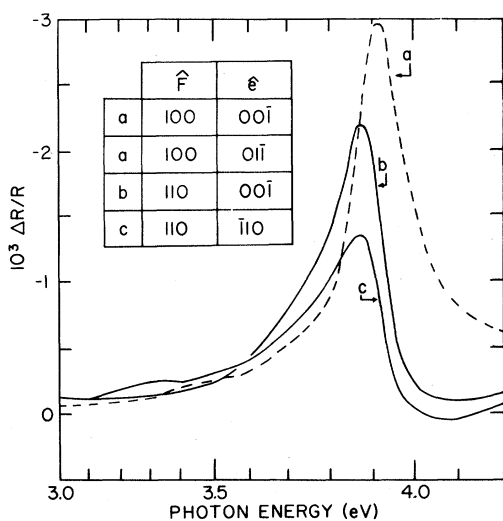
FIG. 1. Normal-incidence electroreflectance of single crystal Ag. The electric field direction $(\hat{F})$ was perpendicular and the polarization vector $(\hat{e})$ was parallel to the surface. Anisotropy is evident only with the field along the [110] direction. Solution, $1M$ KOH; bias, -0.6 V (relative to the SCE); modulation, 0.1 V p-p (relative to the SCE); $f = 1000$ Hz.

The anisotropy observed on the (110) face was not due to s and p polarization effects since the experiment was performed with normally incident light. As an added check the sample was rotated 90° about the vertical to verify that the polarization dependence was following the crystal orientation. The difference in peak magnitude between the two crystal faces in Fig. 1 is characteristic of sample-dependent variations; however, peaks b and c were recorded reproducibly on the same sample.

We have used $1M$ $HClO_4$ as the electrolyte and have tried an etch-attack technique for removing the plastically deformed layer. The shape and polarization dependence of the major structure was independent of solution composition and surface preparation for strain-free, clean, optically smooth surfaces.

The striking dependence of normal-incidence metallic electroreflectance on crystallographic orientation indicates that the electrons in the perturbed region must participate in an interaction with the crystal lattice. This conclusion is reached from a simple symmetry argument. In the undistorted fcc lattice, of $m3m$ symmetry, the dielectric tensor can be diagonalized with all three components of the diagonal equal. The optical properties, which depend on the dielectric

tensor, are isotropic in that case. An electric field establishes a preferred direction which, in the longitudinal configuration, is perpendicular to the sample surface and the polarization vector of the light. The resulting lower symmetry depends on the particular crystallographic face which is exposed. On the (100) face the symmetry is reduced to $4mm$, which is associated with a uniaxial dielectric tensor. However, with the light always polarized perpendicular to the field, the optical properties remain polarization independent. On the (110 face) the symmetry is reduced to $mm2$. The diagonalized dielectric tensor of this symmetry is biaxial and gives rise to polarization anisotropy even in the longitudinal configuration. Our observed data for Ag obey these rules. This firmly establishes the connection of metallic electroreflectance with electrons whose environment has the point-group symmetry of the lattice, and makes a strong case for the participation of modulated interband transitions.

The onset of direct interband transitions near L in bulk silver occurs at 3.87 eV [Fermi surface (F.S.) to s-like states near L],[16] precisely the same energy as the major anisotropic structure in the electroreflectance of the (110) surface. There is no significant reproducible structure beyond 4.0 eV. This behavior suggests a field-assisted interband mechanism which allows absorption through nonvertical transitions at an energy lower than the first interband edge. With a small momentum change such transitions are allowed in silver (F.S. to s-like states at L).[17] In the other noble metals the d-band to F.S. gap is responsible for the onset of absorption. Field-induced indirect transitions are not allowed at this gap since the final states below the Fermi level are already occupied. With this mechanism the d-band to F.S. transition is not modulated.

To test this idea we have performed normal-incidence electroreflectance measurements on the electropolished[18] (110) surface of gold using the technique described earlier. We observe a negative peak at 2.48 eV as reported by other authors[5,6,10] corresponding to the location of d-band to F.S. transitions. As predicted by the field-assisted interband model, this structure was found to be polarization independent. This verifies that the vectoral perturbation is not allowed at the absorption edge of gold. Any modulation of the F.S. to s-like states transition, which may occur at a slightly higher energy, is apparently masked in Au by the stronger unmodulated d-band to F.S. background.

The electroreflectance anisotropy of the inter-band edge in silver may be unique among metals. The onset must occur in an energy region where free-electron effects are small, and must have the proper symmetry to be affected by a longitu-dinal perturbation. In addition, final states must be available to which transitions can occur, with a small momentum transfer, at an energy lower than the direct edge. These criteria are met in silver.

In summary we have studied metallic electro-reflectance on noble-metal single crystals with normally incident polarized light. By employing careful electrochemical techniques, reproducibly clean, unstrained surfaces were produced. We have discovered an anisotropic contribution to the signal on the (110) surface of silver which cannot be explained by previous charge-modula-tion or band-shifting theories alone but can be rationalized by a field-induced vectoral perturba-tion of the joint density of states.

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Stress-Induced Tricritical Phase Transition in Manganese Oxide

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We have performed neutron scattering measurements of the antiferromagnetic order parameter in MnO as a function of temperature and applied uniaxial stress. We find evi-dence for a tricritical point for a stress at about 5 kbar.

Tricritical phase transitions have lately been the subject of many experimental and theoretical investigations.[1] In particular, the field-induced (metamagnetic) phase transitions in the iron hal-ides, $FeCl_2$ and $FeBr_2$,[2] and in dysprosium alum-inum garnet (DyAlG)[3] have provided examples of magnetic tricritical points. These three com-pounds are strongly anisotropic and their behav-