RRR, there was a considerable probability for impurity trapping. Kunz *et al.*[5] found that prequenching enhanced all the substages of stage I except substage I_1. If the prequenching had introduced only vacancies, their results suggest that substage I_1 is associated with close pairs, but not with free migration. If, however, the prequenching had caused dispersion of impurity clusters, the present model does not necessarily contradict their results. At present, we consider that the latter possibility is the case.

In conclusion, it is considered that a free migration of ⟨110⟩ split interstitials occurs at ~15 K in W and ~30 K in Mo and that the other recovery stages at higher temperatures (below room temperature) are probably associated with detrapping of ⟨110⟩ split interstitials which were trapped by various impurity atoms. A detailed account will be published elsewhere.

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Selection-Rule Effects in Electron-Loss Spectroscopy of Ge and GaAs Surfaces*

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Low-energy electron-loss spectroscopy on Ge and GaAs surfaces reveals opticlike selection-rule behavior for transitions involving *d*-core states and empty dangling-bond surface states. From the observed breakdown of these rules at low incident primary electron energies the symmetry of the dangling-bond states may be estimated. The Ga dangling bond is found to be largely *s* like on all surfaces, whereas the Ge dangling bond exhibits *p*-like character on the (111)-(8×8) surface, and mixed *s*-*p* character on the (100)-(2×2) surface.

We present in this Letter new experimental results of low-energy electron-loss spectroscopy (LEELS) on Ge and GaAs single-crystal surfaces which indicate strong primary-energy and surface-orientation dependence for electronic transitions involving core levels and empty localized surface states. It is concluded that the results allow the determination of the symmetry of the final states, information generally not available by other surface techniques.

The experimental details were described previously[1]; however, briefly, low-energy electrons (20–100 eV), from the coaxial electron gun of a cylindrical mirror analyzer (CMA), incident normal to the sample surfaces, are backscattered and detected in a cone of half-aperture of 42.3° by the CMA. The second-derivative spectra were recorded by detecting the second harmonic of the modulation voltage which, in the present case, was reduced to as low as 0.4 V (peak to peak) to achieve an energy resolution of $\lesssim 0.5$ eV.

The (100) and (111) oriented Ge wafers were cut from the same undoped boule ($n \sim 5\times10^{13}$ carriers/cm^3); the GaAs wafers were n-type with carrier concentrations in the low 10^{18}/cm^3. All wafers were chemically polished in a dilute NaOCl solution which left a featureless surface even under interference microscopy at 700×. The surfaces were cleaned by Ar^+-ion bombardment and subsequently annealed. The GaAs surfaces were additionally overgrown by a thin layer of GaAs, using a molecular-beam-epitaxy technique, to assure stoichiometry and to stabilize the surface to contain the desired proportions of As and Ga atoms.[2] Crystallinity and surface reconstructions were monitored by high-energy-electron diffraction. Surface reconstructions, obtained from observations at various azimuths, are indicated in Figs. 1 and 2.

In a previous Letter[1] we have shown and successfully argued that features of the LEELS spectra corresponding in energy to d-core levels in Ge (~30 eV) and GaAs (~20 eV) can be interpreted as arising from transitions from the core states to *empty* conduction-band states and surface states. This interpretation agrees with more recent work on Ge(111).[3] The empty surface states are attributed to the so-called dangling bonds and the loss spectra involving these states exhibit a resonancelike narrow line shape —approximately 0.5 eV wide but probably limited by instrument resolution—which suggests a considerable degree of localization. The latter point is further supported for GaAs by the absence of a loss peak due to transitions from the As d-core levels to the empty, dangling-bond states associated with the Ga atoms.[1]

It is well known that the d-core states of both Ga and Ge are split into levels according to their total angular momentum $j = \frac{3}{2}, \frac{5}{2}$ by spin-orbit interaction, with $d_{5/2}$ lying above $d_{3/2}$. The observed splitting of about 0.6 eV is nearly the same for both atoms,[4,5] and does not change appreciably with their environment. If, furthermore, the dangling-bond states are sufficiently localized so that a description in terms of the

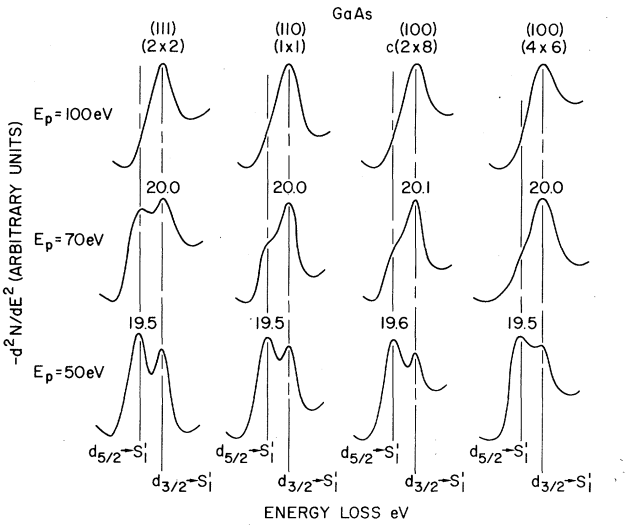

FIG. 1. Loss spectra due to transitions from Ga d-core levels to empty surface states for different primary electron energies and for various GaAs surfaces. The (111)-(2×2) and (100)-(4×6) are polar surfaces composed only of Ga atoms; the (110)-(1×1) and (100)-c(2×8) surfaces are made up of equal numbers of Ga and As atoms (Ref. 6).

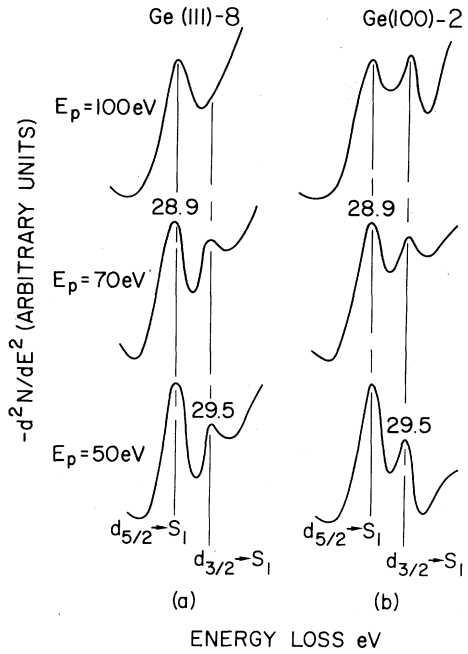

FIG. 2. Loss spectra due to transitions from Ge d-core levels to empty surface states for (a) Ge(111)-(8×8), and (b) Ge(100)-(2×2) surfaces at different primary electron energies.

angular or total angular momentum is valid, one would expect certain selection rules to be operative for the d-core-state–to–surface-state transitions, which depend on the quantum description of both initial and final states.

Such behavior has recently been observed in the loss spectra of GaAs(111), GaAs(110), and GaAs(100) and Ge(111) and Ge(100) surfaces, as shown in Figs. 1 and 2, where we show only the spectral region of interest involving the d-core–to–surface-state transitions. The loss spectra for primary electron energy $E_p = 100$ eV for all GaAs surfaces containing dangling Ga bonds are completely dominated by the 20.0-eV structure, which corresponds to the excitation $d_{3/2} \rightarrow S_1'$ from the lower of the spin-orbit split d levels to the highest lying surface state S_1'. The fact that the $d_{5/2} \rightarrow S_1'$ transition is not detected is particularly interesting in view of the fact that this transition, if allowed, should be greater than the $d_{3/2} \rightarrow S_1'$ by a ratio of 3:2. The sensitivity of measurement limits the intensity of the $d_{5/2} \rightarrow S_1'$ transition to be less than 20% of that of the $d_{3/2} \rightarrow S_1'$ transition and indicates that the former is largely suppressed for $E_p \gtrsim 100$ eV.[7] A similar suppression of the $d_{5/2} \rightarrow S_1'$ transition was observed recently by a photoemission partial-yield technique.[8] Although this structure was still resolved, its intensity was only about 20% of that expected based on the population of the $d_{5/2}$ level. No significance was attached to the observed discrepancies.

At this point it is convenient to try to make contact with optical selection rules. It is, of course, well known that at high primary electron energies, inelastic scattering by both free atoms[9] and solids[10] can be described in terms of optical transitions, a direct outgrowth of the validity of the first Born approximation. The lower range of validity of this approximation has not been determined for solids, but has been estimated for some excitations in a few atomic species, predominantly for hydrogen and lighter noble-gas atoms.[9,11] Since, even for the same atom, the lower energy range of validity of the Born approximation varies with the type of excitation, it is difficult to establish any generalities. From a casual search of the available data it seems that $E_p \sim 100$–200 eV is the lowest energy range where one could expect the first Born approximation to be valid. At lower energies higher approximations must be considered which rapidly increase the probability for the occurrence of optically forbidden transitions. Of these the quadrupole transitions are the most important. At low primary electron energies severe potential distortions occur in the atom because of the presence of the extra electron. This distortion not only enhances the admixture of different electronic states, and hence the possibility for the quadrupole transitions, but allows for the possibility of electron capture and emission which may be accompanied by a spin flip. This latter exchange interaction is largely responsible for the excitation of triplet states. Large-angle scattering further enhances the relative strength of forbidden transitions over optically allowed transitions.[9,11]

With these considerations, we can argue that the appearance at lower E_p of the $d_{5/2} \rightarrow S_1'$ transition for GaAs in Fig. 1 is the result of the breakdown of the optical (dipole) selection rules $\Delta J = 0, \pm 1$, and that at 100 eV and above an optical description is still adequate.[7] We may postulate that the surface state obeys predominantly a $j = \frac{1}{2}$ description, which, most generally, indicates an admixture of $s_{1/2}$ and $p_{1/2}$ states. There may be some objection to a total-angular-momentum description of the surface state. An alternative explanation is to assign the allowed $d_{3/2} \rightarrow S_1'$ transition to a spin-flip ($\Delta S = 1$) transition, allowed because of spin-orbit interactions; the spin flip assures that parity is changed, a requirement for dipole transitions. Either description indicates the other $d_{5/2} \rightarrow S_1'$ transition to be a quadrupole transition, observable only for low primary electron energies. A predominantly s-like description of this surface state is also plausible from the bonding point of view: The three Ga valence electrons are largely involved in covalent bonds with surrounding As atoms, leaving the remaining dangling bond empty, which from energetic considerations should be largely s like.

The situation for Ge is entirely different. The LEELS spectra at 100 eV for the (111)-(8×8) surface [Fig. 2(a)] indicates only the lower or $d_{5/2} \rightarrow S_1$ transition. As was the case with GaAs the other forbidden transition emerges out of the background as E_p is lowered, but remains considerably weaker than the $d_{5/2} \rightarrow S_1$ transition.

These results again suggest that transitions above 100 eV obey optical selection rules and thus the final state should correspond to a $j = \frac{3}{2}$ or p-like description. In this case $d_{3/2} \rightarrow S_1$ is also an allowed transition. However, it can be shown that the relative intensity for a d-p level transition involving no change in total angular

momentum (i.e., $j=\frac{3}{2}\rightarrow j=\frac{3}{2}$) is expected to be an order of magnitude weaker than a corresponding $j=\frac{5}{2}\rightarrow j=\frac{3}{2}$ transition.[12,13]

This p-like character of the dangling bond is also expected from a bonding point of view: The surface atoms are assumed to be pulled towards the second layer because of the increased strength of the back bonds, forcing the tetrahedrally coordinated surface atoms into a more planar-trigonal coordinated arrangement. This arrangement is better described in terms of sp^2 orbitals, which changes the character of the dangling bonds from sp^3 to a p_z-like description. The lateral strain in the surface layer due to the contraction is believed to be relieved either by the creation of vacancies[14] or by buckling of the surface layer.[15]

The Ge(100) surface [Fig. 2(b)], on the other hand, clearly exhibits both $d_{5/2}\rightarrow S_1$ and $d_{3/2}\rightarrow S_1$ transitions even above 100 eV.[7] It is concluded that S_1 for this surface is an admixture of both s- and p-like orbitals of roughly equal proportions. This assignment does not agree with a proposed p_y or p_z assignment for the unreconstructed surface using a tight binding method.[16] However, most models of the reconstructed (100) surface favor a pairing of surface atoms[14,17,18] which suggests the formation of double bonds. These are expected to be of hybrid, s-p-like character somewhat analogous to a molecular double bond.

The observation that only the $d_{5/2}\rightarrow S_1$ transition is allowed for high energies in LEELS on the Ge(111)-(8×8) surface is at variance with results obtained by the photoemission partial-yield technique[8] on the cleaved Ge(111) surface, which indicates that the $d_{3/2}\rightarrow S_1$ transition is seen as well. Two major reasons may be cited for this discrepancy: (a) The cleaved surface, assumed to be a (2×1) reconstructed surface, differs from the annealed (111) surface not only in surface reconstruction, but also in the distribution of the electronic surface states which affects the work function[19] and the chemical reactivity[20]; and (b) a generally large cleavage-step density[21] results in a significant number (~20–30%) of surface atoms to be at edge locations or otherwise be differently coordinated than the ideal (111) surface atom. These would contribute to an admixture of s-like character to the dangling bond, as observed on the (100) surface. The fact that both transitions are observed by LEELS on Ge(100), in itself, indicates that there is a strong orientational dependence of the nature of the dangling-bond surface states, which cannot be ascribed to relativistic effects or variations in wave-function overlaps, but can readily be explained from symmetry arguments. Cleavage steps are not expected to affect the symmetry of the Ga dangling bonds, since their symmetry was observed not to depend on crystallographic orientations.

In summary, we have shown by LEELS that the empty dangling-bond states of GaAs and Ge(111)-(8×8) exhibit dominant s- and p-like character, respectively, whereas that of the Ge(100)-(2×2) surface consists of an admixture of these two.

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Excitation Functions for the Reactions $^{12}C(\pi^{\pm}, \pi N)^{11}C$ over the Region of the (3,3) Resonance*

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The excitation functions for the reactions $^{12}C(\pi^{\pm}, \pi N)^{11}C$ have been measured by activation over the energy ranges 50 to 470 MeV for π^+ and 40 to 550 MeV for π^-. These excitation functions, clearly reflecting the (3,3) pion-nucleon resonance, show an upward energy shift in the resonance peak for π^- and a downward shift for π^+. The $\sigma_{\pi^-}/\sigma_{\pi^+}$ ratio at 180 MeV is 1.55 ± 0.10.

The observation by Chivers *et al.*[1,2] in 1968 that the cross sections for the formation of ^{11}C from ^{12}C by π^+ and π^- near the (3,3) resonance energy (180 MeV) are the same within ± 10% aroused considerable theoretical interest because, on the basis of the free-particle pion-nucleon cross sections and a simple nucleon knockout model, a $\sigma_{\pi^-}/\sigma_{\pi^+}$ ratio near 3 was expected. This apparent puzzle together with the serious discrepancies among the several reported measurements[2-6] of the cross sections for the π^+-induced reaction (see Fig. 1) provided the incentive for remeasuring these cross sections. Also, the need to establish the reaction $^{12}C(\pi^{\pm}, \pi N)^{11}C$ as a foil-activation flux monitor for pion beams, in analogy with the widely used reaction $^{12}C(p, pn)^{11}C$ for proton beams, called for a careful remeasurement of the excitation functions for the formation of ^{11}C by π^+ and π^- over the energy range available at the Clinton P. Anderson Meson Physics Facility (LAMPF).

Since the present results for the π^+ cross sections above ~ 120 MeV differ considerably from earlier measurements, we will describe the experimental techniques in some detail.

The method used to determine the cross sections consisted of a direct measurement of the total number of pions passing through a three-element scintillation-counter telescope during the irradiation of a plastic scintillator target placed directly in front of, and of the same size as, the first element of the telescope. The ^{11}C activity induced in the target was determined after the irradiation by β^+-γ coincidence counting.

The irradiations were carried out at the low-energy pion channel (LEP), 15 m long, and at the high-energy pion channel (P^3), 20 m long, of LAMPF, the former being used for pion energies between 50 and 220 MeV, the latter for energies between 100 and 550 MeV. At least duplicate determinations were made at each reported pion energy, usually at beam intensities that differed