Investigation of Intrinsic Unoccupied Surface States at GaAs(110) by Isochromat Spectroscopy

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Bremsstrahlung isochromat spectroscopy has been employed to measure the density of unoccupied electronic states on GaAs(110). The experiment was carried out at a quantum energy of 70 eV, resulting in a maximum of surface sensitivity. The theoretically predicted empty surface states B_1', S_1', B_2', and S_2' are identified. Their energetic positions as well as relative strengths are in excellent agreement with calculations based on the bond-relaxation model. A binding energy of 1.0 eV for the Ga 3*d* surface exciton is obtained.

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Intrinsic empty electronic surface states are well known to exist in or near the fundamental gap of various semiconductors.[1,2] The first direct observation of such states on GaAs(110) was reported by Eastman and Freeouf[2] who, applying the technique of partial-yield spectroscopy, found an unoccupied surface state in the fundamental gap apparently in agreement with observed Fermi-level pinning. Subsequent careful work-function measurements as a function of surface defects,[3] however, lead to the conclusion that Fermi-level pinning on GaAs(110) surfaces is always due to defect-induced extrinsic surface states. The partial-yield spectroscopy measurements by Eastman and Freeouf could therefore only be interpreted by assuming a surface exciton with the unusually high binding energy of approximately 0.5 eV. A recent careful analysis of bulk-to-surface core-level shifts by Eastman *et al.*[4] indicated a lower bound of 0.8 eV for the Ga 3*d* exciton binding energy. The exact energetic position of the empty electronic surface states on GaAs(110) is therefore of continued interest. Since any spectroscopic method relying on core-level excitation will suffer from excitonic effects and yield at best an estimate of the binding energy, we have designed an isochromat experiment which should reveal the true energetic position of empty electronic states with respect to the bulk conduction band minimum (CBM).

In isochromat spectroscopy, the sample under investigation serves as the anode of an x-ray tube. The emitted bremsstrahlung is recorded with an energy-selective detector of pass energy $\hbar\omega_0$ as a function of the accelerating voltage across the tube. The radiative process may be most simply described as an inverse photoelectric effect.[5,6] Those electrons with initial energy E with respect to the Fermi level of the anode which undergo a radiative transition with emission of an x-ray quantum $\hbar\omega_0$ will occupy final states at an energy $E-\hbar\omega_0$ in the conduction band of the sample. Neglecting a possible energy dependence of the transition matrix element, the transition rate will be directly proportional to the density of empty final states. The density of empty one-electron states can therefore be scanned simply by varying the incident electron energy.

The experimental setup in this work employs a soft-x-ray appearance-potential spectrometer with an aluminum foil in front of the photocathode. The thickness of the foil is chosen such that radiation with energy immediately above the L_{III} absorption edge of aluminum at 72.7 eV is almost completely absorbed. The harmonic modulation of the potential applied to the sample sweeps the x-ray spectrum periodically across the absorption edge. As has been shown elsewhere in detail,[7] the first harmonic of the measured photocurrent as a function of electron energy yields the isochromat corresponding to a detector energy equal to the energy of the absorption edge. In order to obtain a maximum of surface sensitivity, the aluminum L_{III} absorption edge was chosen in this work.

The lightly doped *n*-type GaAs(110) sample was prepared by ion bombardment and annealing. Measurements were taken in 0.25-eV intervals, the total charge per point being 15 mC. The results are shown as solid dots in Fig. 1. Since the emphasis was on structural peculiarities rather than best fit in the least-squares sense, the data were analyzed employing the *r*-factor concept developed by Zanazzi and Jona.[8] A hypothetical surface density of states $N_h{}^s$ was constructed consisting of four surface states

$$N_h{}^s=\sum_{i=0}^{3}A_i N^s(E-E_i),\quad \sum_{i=0}^{3}A_i=1, \tag{1}$$

where N^s is the density of states (DOS) as cal-

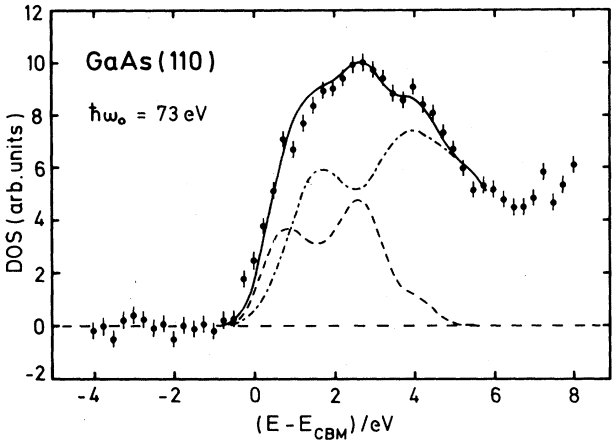

FIG. 1. Solid dots represent the measured isochromat. The full line is the density of states (DOS) derived in this work. The surface and bulk contributions are shown as dashed and dash-dotted lines, respectively.

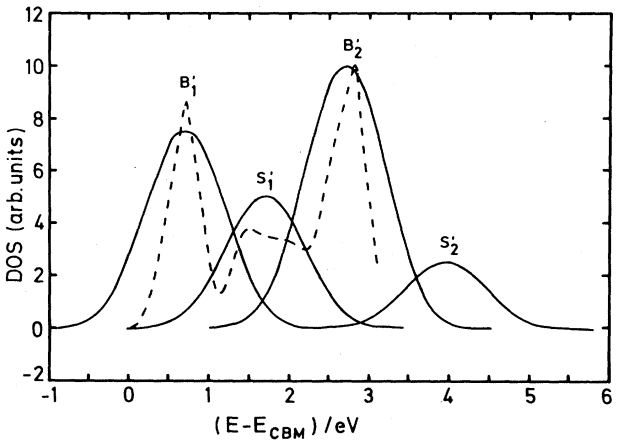

FIG. 2. The surface contribution to the observed density of states is decomposed into individual surface states. The dashed line is the (unbroadened) result of Chadi's calculation based on the bond-relaxation model, shifted by 0.4 eV to lower energies.

culated for the B_1' state by Chadi[9] for the bond-relaxation model of Kahn *et al.*[10] A bulk contribution N_B as obtained from empirical nonlocal pseudopotential calculations[11] was then added to $N_h{}^s$ yielding the total DOS,

$$N_h = QN_B + (1-Q)N_h{}^s. \quad (2)$$

Finally, to account for the finite amplitude of the potential modulation and the thermal electron energy spread, N_h was broadened accordingly. A minimum ($r = 0.18$) of the r factor from a comparison of (2) with the experimental data indicated the optimum choice of the parameters. The result of this analysis is shown as the solid line in Fig. 1. The dashed and dash-dotted lines represent the surface and bulk contributions $(1-Q)N_h{}^s$ and QN_B, respectively. As expected, because of the small penetration depth of 70-eV electrons, almost 50% of the observed signal is contributed by the surface states.

In Fig. 2, we have decomposed this surface contribution into the individual surface states. The dashed curve represents the theoretical calculation by Chadi[9] based on the bond-relaxation model of Kahn *et al.*[10] The agreement between Chadi's calculation and the result of our analysis is considered to be excellent as far as relative positions and intensities of the B_1', S_1', and B_2' states are concerned. The S_2' state has been mentioned by Chadi[9] to be 2.9 to 3.4 eV higher than the B_1' state. More recently, an energy difference of 3.05 eV was given with a strength similar to S_1'.[12] This figure compares favorably with our 3.25 eV. Positions and strengths of calculated surface states have been shown to respond very sensitively to the kind of surface relaxation on which the calculation is based.[9] The present results therefore lend strong support to the bond-relaxation model of Kahn *et al.*,[10] also favored by low-energy electron-diffraction results. This is also in accordance with recent findings of Ludeke and Ley,[13] who also found best agreement of their valence-band surface-state measurements with the theoretical density of states obtained for this model.

Since in our experiment it was not yet possible to determine independently the energy of the CBM, the energy scale in Figs. 1 and 2 has been chosen to coincide with the CBM position given by Chelikowsky and Cohen[11] for the bulk density of states. On this basis, it is possible to give a new independent value for the Ga $3d$ surface exciton binding energy: Partial-yield measurements result in a Ga $(3d_{5/2})$ to surface exciton transition energy of 19.68 eV[4]; i.e., they place the B_1' surface state at 0.3 eV below CBM [or at 0.6 eV below CBM if the surface binding energy of the Ga $(3d_{5/2})$ level is used[4]]. Our analysis instead indicates 0.7 eV above CBM, yielding an excitonic binding energy of 1.0 eV [or 1.3 eV] in agreement with the recent estimate by Eastman *et al.*[4]

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Influence of Superconductivity on Crystal Electric Field Transitions in $La_{1-x}Tb_xAl_2$

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Inelastic neutron scattering from the crystal electric field transitions in $La_{1-x}Tb_xAl_2$ single crystals has revealed an abrupt increase in the lifetimes of these transitions when the system becomes superconducting. An increase in the integrated intensities is also observed. The lifetime effects are quantitatively reproduced by existing theories, which take into account the reduced scattering of the conduction electrons by the magnetic ions due to the creation of the superconducting energy gap $2\Delta(T)$.

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Dilute magnetic ions embedded in a sea of conduction electrons constitute a problem in solid-state physics which has attracted much attention over the years. The mutual interactions affect the transport properties and, at low temperatures, give rise to the Kondo effect in normal metals and pair breaking in superconductors.[1] The same interactions are the mediators of the indirect Ruderman-Kittel-Kasuya-Yosida exchange between the magnetic ions; hence, they constitute the microscopic origin of the wealth of cooperative magnetic phenomena which are found in rare-earth (RE) metals and alloys. In the low concentration range the interplay between the tendencies towards magnetic ordering and towards superconductivity is particularly intriguing, with possibilities for the formation of spin-glass states.[2]

It is therefore of interest to seek a more detailed understanding of the coupling mechanism between the conduction electrons and the localized moments. In this Letter we report the first inelastic neutron scattering experiment that clearly shows the effect of superconductivity on the excitation spectrum of the magnetic impurities.

We have studied the crystal electric field (CEF) transition in Tb^{+3} ions dissolved in $LaAl_2$. The samples were single crystals of about 12 cm^3 grown by a Gzochralski method.[3] The Tb concentrations in the two samples of $x = 0.001$ and $x = 0.003$ were checked by magnetization measurements. Pure $LaAl_2$ is a weak superconductor[4] and the addition of Tb^{+3} impurities lowers T_c from 3.16 to 3.1 K and 2.6 K for the 0.1% and

