Observation of the Real Li *K* Absorption Edge

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(Received 17 July 1975)

The Li *K* absorption edge was measured with yield spectroscopy at liquid-nitrogen temperature. The broad feature hitherto considered to be the edge is shown to be a combination of a sharp absorption edge corresponding to a 0.17-eV-wide Li *K* core level and a rising density of states at the Fermi level.

The shape of the Li *K* absorption edge has been extensively discussed since it was first observed in 1937.[1] Theoretical interest was caused by the strong deviation of both the Li *K* emission and absorption edges from the expected sharp Fermi step. Several approaches to the Li-*K*-edge problem have been made[2-7] among which the final-state-interaction theory put forward by Mahan, Nozières, and de Dominicis (MND) is presumably the most attractive.[3,4]

This many-body theory predicted a rounding of the Li *K* edge and thus seemed to explain both the similarity of emission and absorption edges and their considerable width. The interpretation of various edge data in terms of this theory has recently been criticized by Dow and co-workers in a series of papers.[7-10] Tests of the theory (dependence of the edge shape on momentum transfer[11] and temperature[12]) have been performed and did not follow the predictions, thus casting doubt on the explanation of the edge shapes by the MND final-state-interaction theory.

An alternative to the MND theory is a simple one-electron band theory. The transition density for Li *K* absorption was calculated in great detail by McAlister.[5] This density is virtually a product of the matrix element and the p-symmetric part of the conduction states, which is sampled by the absorption process from the s-like inner shell. Because of the hitherto observed broad structureless absorption threshold[1,11-15] this one-electron model appeared to be inappropriate. It was maintained by Dow, Robinson and Carver[7] that in the framework of the one-electron theory the observed threshold shape could be fitted under the assumption of an extreme $1s$-core-level width of about 0.5 eV. An electron-phonon interaction mechanism which would produce such a width was proposed[7]; exact calculations, however, have not yet been reported. It is shown in this Letter that the Li *K* absorption edge when observed at liquid-nitrogen temperature (LNT) has a shape which allows for a straightforward single-electron explanation.

Measurements of the partial photoyield of massive specimens of Li were performed under ultrahigh-vacuum conditions. The photoyield was shown to be proportional to the absorption coefficient in the vacuum ultraviolet except for the shape of a smoothly varying background.[16] In the edge region up to 2.49 eV [17] above the edge (work function) the Auger decay of the core hole is practically the only primary process contributing to the photoyield. It is proportional to the absorption coefficient of Li. Synchrotron radiation and a special monochromator with a fixed exit beam[17] served as a light source. More details are given in Ref. 12. The only change in the experimental setup described there was a modification of the sample holder permitting measurements at LNT. The measured sample temperature was 79 K.

Figure 1 shows two of the original photoyield spectra which led to the interpretation of the Li *K* absorption threshold given here. The results have very recently been confirmed in a remeasurement which also involved temperature dependence by Kunz and the author. The data obtained in that total-yield experiment are of far better statistics and will be published elsewhere.[19] Judging, however, from the observed optimum edge-height-to-background ratio (6:1), the samples investigated here contain by far less oxygen than those in the remeasurement.[19] Although in that case the oxygen content of the sample appeared not to be a decisive factor, it could well be that high concentrations add to the blurring of the Li edge. Moreover, different from the remeasurement, the Li samples in the partial-yield measurement discussed here were generated by solidification from the liquid phase under ultrahigh vacuum conditions (~ 10^{-10} Torr). Therefore they must have long-range order.

In spite of the rather poor statistics, the curves presented in Fig. 1 clearly exhibit a steep rise at

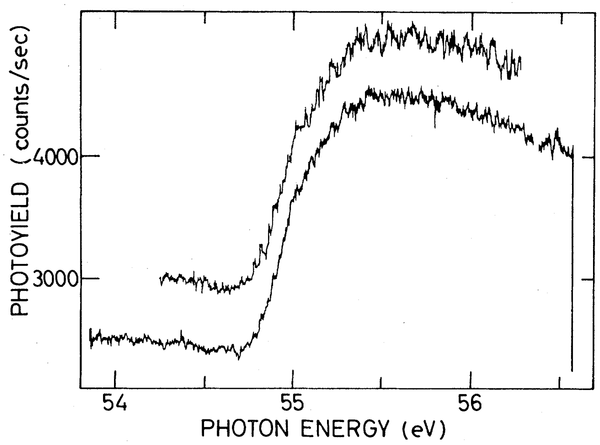

FIG. 1. Li K absorption edge measured with yield spectroscopy at LNT; original x-y recorder trace obtained with counting technique and rate meters. The time constant was 0.3 sec. The upper curve is displaced for clarity with respect to the y axis.

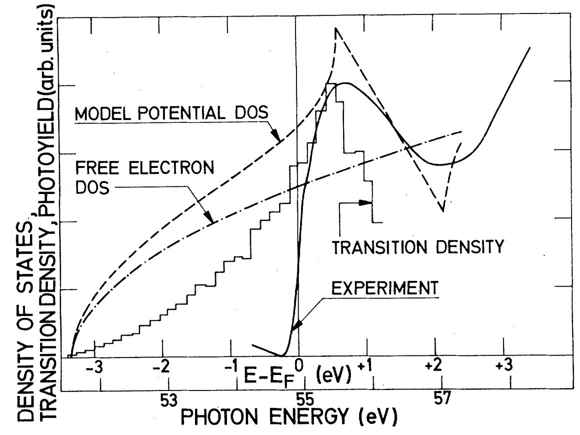

FIG. 2. Li K absorption edge measured with yield spectroscopy at LNT. Included is the free-electron DOS and the model-potential DOS calculated by Shaw and Smith (Ref. 20). The 3.32-eV Fermi energy was reported by Lee (Ref. 21) and differs from the free-electron value by a factor of 0.856 (Ref. 20). Also shown is the transition density to p-symmetric final states as calculated by McAlister (Ref. 5).

the onset followed by a significant decrease of slope. The bend observed at 55 eV photon energy cannot be explained by the MND theory^{3,4} or by core-level broadening^{7} but it finds a suggestive explanation in the shape of the transition density^{5} and the model-potential density of states (DOS)^{20} shown in Fig. 2. It is therefore argued that the Li K absorption edge extends from the onset of absorption to the bend and is followed by DOS structure.

Figure 2 shows that the Li K absorption edge at LNT, the model-potential DOS calculation by Shaw and Smith,^{20} for comparison their free-electron DOS, and McAlister's calculation^{5} of the transition density to p-symmetric final states. In the relevant energy interval ($E_F \leq E \leq E_F + 0.5$ eV) the transition density should be approximately proportional to the p-symmetric DOS since a possible variation of the matrix element should be small. The predominantly p-symmetric character of the eigenfunctions near the Brillouin zone boundary is reflected by the excellent agreement between the model-potential DOS and experiment concerning the positions of the extrema. The inadequacy of the free-electron DOS is obvious.

Figure 3 shows a fit to the Li K edge. The Cs N_5 absorption edge included in this figure will be discussed below. The Li experimental curve was derived from five experimental curves. The dashed line represents the convolution of a piecewise-linear transition density and a Gaussian distribution with $\Gamma = 0.086$ eV corresponding to 0.20 eV full width at half-maximum. As Fig. 3 demonstrates the transition density used for the best fit differs only slightly from the general shape of McAlister's calculation.^{5}

Under the tentative assumption of a quadratic

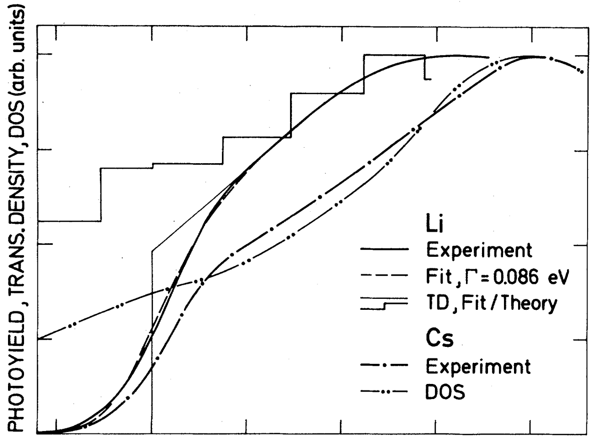

FIG. 3. Li K and Cs N_5 (Ref. 22) absorption edges as measured with yield spectroscopy at LNT. Included is the transition density (TD) calculated by McAlister (Ref. 5) and a fit to the Li K edge (see text). The position of E_F (Li) corresponds to 54.87 ± 0.05 eV photon energy. Also shown is the calculated p-symmetric DOS of Cs (Ref. 23). The position of E_F (Cs) corresponds to 77.1 ± 0.1 eV photon energy (Ref. 22).

superposition of the resolution function of the monochromator (~ 0.11 eV full width at half-maximum at 55 eV) and contributions to the edge width inherent in Li, a Li K-core-level width of about 0.17 eV is obtained. A width of this order of magnitude can almost be explained by Auger lifetime braodening alone; a lower bound of this effect was calculated to be 0.13 eV.[24] A weak rounding of the transition density in the edge region due to the MND many-body effect[3,4] cannot be excluded. It might be reflected by the steeper slope of the experimentally observed transition density compared to McAlister's calculation.[5]

The Cs N_5 absorption edge, which was recently measured by the author,[22] is included in Fig. 3 to show a striking analogy to the Li K edge: In both cases p-symmetric final states are involved and in both cases a bent threshold is observed which is in agreement with one-electron band theory.

Influence of oxide, other impurities, or lack of long-ranged crystalline order are possible explanations for nonobservation of the bend in the electron-energy-loss experiments by Ritsko, Schnatterly, and Gibbons[11] and in the LNT absorption measurements.[13] In the latter the exponential distortion of the absorption coefficient in the original spectra is an unfavorable factor for the observation of such a small effect. However, the absorption data obtained at LNT (see Fig. 4 of Ref. 15) already show some asymmetry in the threshold shape. A discrepancy between the result obtained by the technique of yield spectroscopy compared to a true absorption measurement is not expected to occur in the region below the vacuum level of Li where directly excited electrons cannot escape the material. Correspondence of yield and absorption has now been observed for a considerable number of substances, see, e.g., Gudat, Kunz, and Petersen.[25] Moreover, the absorption data obtained at LNT agree with the present LNT yield data concerning the steep rise at the onset, and our room-temperature data[12] are in good agreement with those of Ritsko, Schnatterly, and Gibbons.[11] In order to explain the present result as an artifact of the measuring technique a mechanism would therefore be required which only influences yield spectroscopy and this only at low temperatures, again a very improable assumption.

The fit of Ritsko, Schnatterly, and Gibbons to their data obtained at room temperature (see Fig. 5 of Ref. 11) is not very good in the upper region of the edge and could be an indication of the bend even in the room-temperature data. Their data obtained at 160 K, which are more appropriate for comparison with our curve, are unfortunately not shown in Ref. 11. The large width and the symmetric shape as reported for that curve differ considerably from both photoabsorption[15] and the present photoyield data obtained at LNT. The origin of this difference is not yet understood; it can only partly be attributed to the higher temperature.[12]

The experimental results demonstrate that the Li K absorption edge at LNT can now be interpreted essentially in terms of one-electron band theory. The width of the edge is in qualitative agreement with calculations of lifetime broadening due to the Auger KVV decay of the $1s$ core hole. A weak rounding of the transition density due to MND final-state interaction[3,4] cannot be excluded, but a possible contribution of this effect to the edge width must have a value far less than 0.1 eV. Core-level broadening caused by lattice relaxation (~ 0.06 eV at LNT)[6] might be involved in the edge width. The assumption of a large core-level width due to indirect electron-phonon interaction[7] is obviously unnecessary. The previously observed broadening at higher temperatures[12] has to be reinterpreted in the light of this new result and will be extensively discussed elsewhere[19] together with other implications of the present result.

The author is grateful to C. Kunz and B. Sonntag for stimulating and fruitful discussions. He is indebted to C. Kunz for his strong personal support.

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Exciton Energy Transfer in GaP:N

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(Received 2 September 1975)

Energy transfer of bound excitons in GaP:N is investigated by time-resolved, resonant-excitation spectroscopy and by studies of below–band-gap excitation spectra. Exciton tunneling is found to dominate over dipole-dipole interactions because of the large spatial extent of the exciton wave function. This is the first definitive observation of exciton tunneling in a semiconductor.

The mechanisms by which localized excitations move through a solid are of interest to various branches of solid state physics. An important example occurs in some laser materials where the dipole-dipole interaction is usually responsible for energy transfer.[1] In III-V semiconductors, "concentration quenching" of shallow bound excitons gives evidence of energy transfer,[2,3] but until now this has not been the subject of full investigation.[4] We show that in GaP:N, transfer can occur over distances an order of magnitude greater than in insulating laser materials. The difference originates from the very large extent of the exciton wave function, which allows tunneling to dominate over the dipole-dipole interaction.

In GaP:N, the isoelectronic impurity nitrogen binds excitons both to the isolated N atom (*A* and *B* excitons) and to near-neighboring nitrogen pairs (NN_i excitons). A series of about ten distinct bound-exciton levels may be observed in luminescence and absorption spectra.[2] The N concentrations of our samples were found from the absorption strength of the *A* line, using the calibration of Lightowlers, North, and Lorimer[5] and NN pair densities were calculated assuming a random distribution. No evidence for emission originating from any other impurity center was found; thus we conclude the unwanted impurity level to be $\sim 10^{16}$ cm^{-3} or less.

For N concentrations above about 10^{18} cm^{-3}, the emission shifts progressively into the lower-energy NN-pair lines. This behavior is clearly seen in published spectra[2] of GaP:N, and examples are shown in Fig. 1 for two samples having N concentrations differing by an order of magnitude. The changing statistical concentration of NN pairs cannot explain this quenching; in the heavier doped sample *V*59, the NN pairs that dominate the emission (Fig. 1) account for less