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by

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Optical Excitation of the Rb^+4p-Level in Rubidium Halides at 8 K[f]

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In the 15-19 eV range new spectral features have been resolved in the reflection spectra of RbCl, RbBr, and RbI single crystals. They are not entirely consistent with results of a recently proposed ligand field model for the Rb^+4p-excitons.

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A pronounced multiplet structure has been observed in the optical spectra of Rb halides around 17 eV by measuring either the reflection[1,2] or the absorption[3] for temperaturesdown to that of liquid nitrogen. The multiplets were associated with localized excitonic transitions from the outer 4p-shell of the Rb^+ ion, because their main components lie close to the energies of the lowest excited states of the free Rb^+ ion[1,3]. In order to improve the simple ionic model which predicted five low lying dipole allowed transitions (two to final states with $4p^5 5s$ configuration and three with $4p^5 4d$ configuration), a more sophisticated localized model based on ligand field theory has recently been proposed by Satoko and Sugano[4]. This model seemed to be capable of describing the details of the hitherto observed multiplet structure in a more quantitative way as regards energy position and oscillator strength of the various transitions.

We have measured the reflectivity of Rb halide single crystals down to 8 K in order to check the validity of the ligand field model. One of our goals was the detection of some extra lines predicted by this model and the investigation of the behavior of oscillator strength at considerably lower temperatures than applied before. In our experiment, the synchrotron radiation of the DESY electron synchrotron was used, together with a normal-incidence monochromator providing a resolution of 2 Å ≙ 40 meV[5]. The single crystals were freshly cleaved in air and then immediately transfered to a reflectometer in an ultrahigh-vacuum-sample-chamber. Figures 1 and 2 show the experimental results. The absolute reflectivities of the highest peaks at room temperature were approximately 10 %. In the spectra of the absorption coefficient obtained by Kramers-Kronig analysis from the reflectivity data no remarkable changes in the relative heights and positions of the peaks were found. The spectrum of RbCl and its temperature dependence look very similar to that of RbBr.

Moreover, many of the prominent features observed in the spectra of all three halides can easily be related to each other; a more difficult problem is the understanding of the origin of the lines in a single spectrum.

In comparison to the dipole allowed five transitions according to the simple ionic model, nine low-lying nondegenerate terms are expected in the ligand field model. Two of them correspond to a $4p^5 5s$ configuration, four to a $4p^5 4d\varepsilon$ and three to a $4p^5 4d\gamma$ configuration. By taking into account Coulomb-, spin-orbit and ligand-field interaction the term energies were calculated as a function of the crystal field parameter Dq including configuration mixing of the nine terms. For comparison with the experiment the levels were designated by I, II, III, IV ($p^5 d\varepsilon$), A,B($p^5 s$) and C,D,E($p^5 d\gamma$).[4] The above sequence also gives the calculated order of term energies starting with the lowest level denoted by I. The most prominent peaks in the spectra observed at liquid nitrogen and room temperature were attributed to A,B,C,D,E (see Figs. 1 and 2). At these temperatures their positions and oscillator strengths agree fairly well with the calculations.

However, our data at 8 K show additional clearly resolved structures X and Y between A and E which do not fit the assignments given by Satoko and Sugano. In their model no extra level should be located between A and E. Furthermore, there is a characteristic reversal of intensity associated with A and B in the case of RbI. From room temperature to 8 K the ratio of the peak heights of A and B changed from 1.7 to 0.9. The same reversal was also detected in the reflection spectrum of an evaporated RbI film at 10 K. This reversal does not agree with oscillator strengths calculated by means of the ligand field model.

At temperatures as low as 8 K no excitations could be identified which were unambiguously attributable to the predicted weak quartet I-IV at low energies arising from the $p^5d\varepsilon$ configuration. However, it was noticed that for RbI the broad peak below A-B observed at 15.8 eV for liquid nitrogen temperature is split into two lines U-V at 8 K. It is not clear whether these peaks are members of the quartet I-IV. It may also be possible that the quartet is still hidden by some prominent excitations due to transitions from the valence band.

Although the ligand field model proposed by Sugano and Satoko seems to be a very promising approach, in its present form, it cannot account for the new features observed around the onset of the Rb^+4p excitation in Rb halides well below liquid-nitrogen temperature. For the improvement of quantitative results of that model it seems necessary to use a different set of parameters connected with a possible change of certain assignments.

Figure Captions

Fig. 1 Reflectivity spectra for 7.5° angle of incidence of RbCl and RbBr single crystals at 8 K (solid lines) and room temperature (dashed lines). Structure due to Y in RbCl shows up in an additionally performed wavelength modulation spectrum. The vertical bars indicate energies and oscillator strengths in the ligand field model (Ref. 4).

Fig. 2 Reflectivity spectra for 7.5° angle of incidence of a RbI single crystal at 8 K (solid line), at liquid nitrogen (dash-dotted line) and room temperature (dashed line). The vertical bars indicate energies and oscillator strengths in the ligand field model (Ref. 4).

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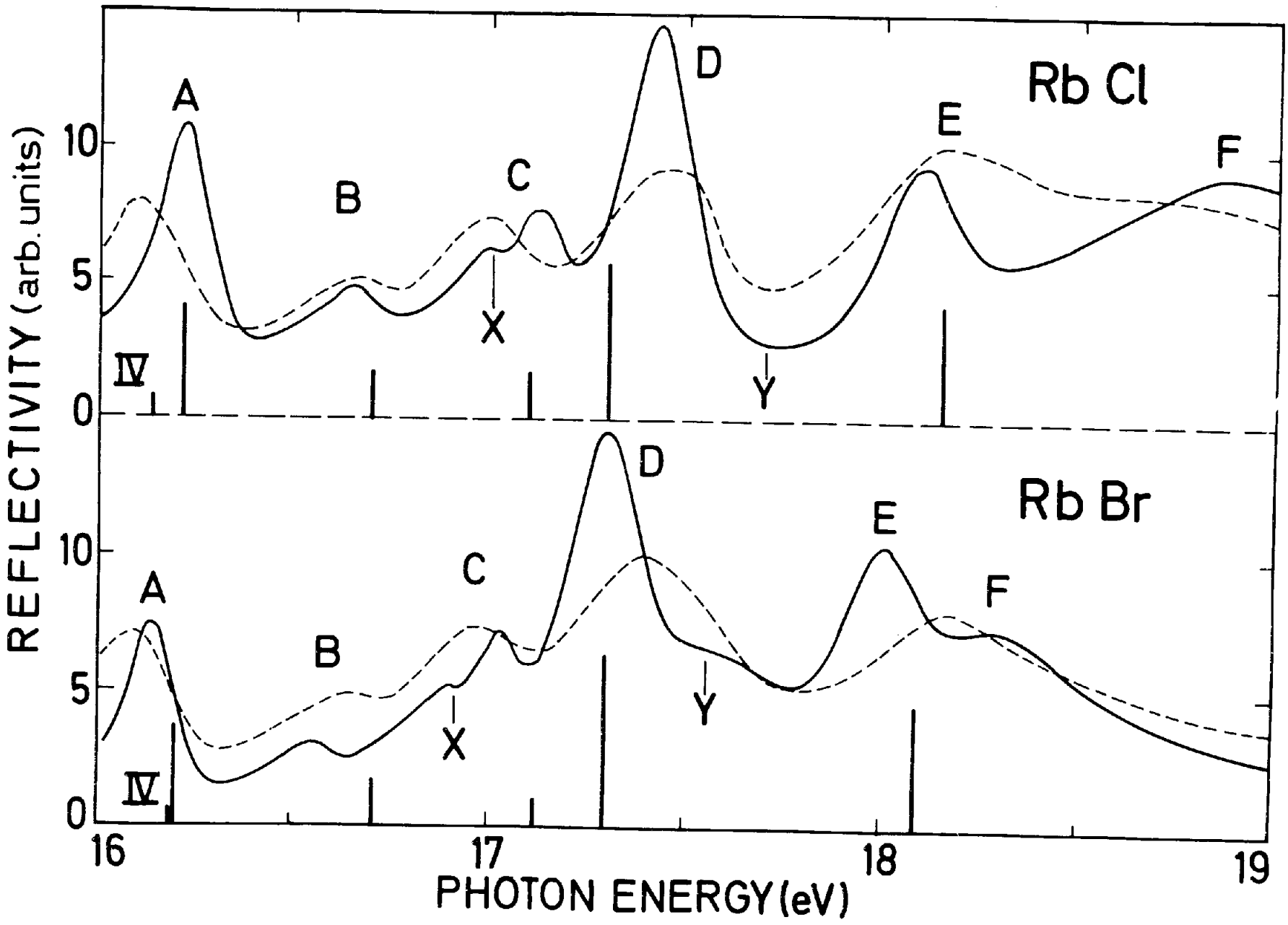
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Rb Br
A
B
C
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Ⅳ
REFLECTIVITY (arb. units)
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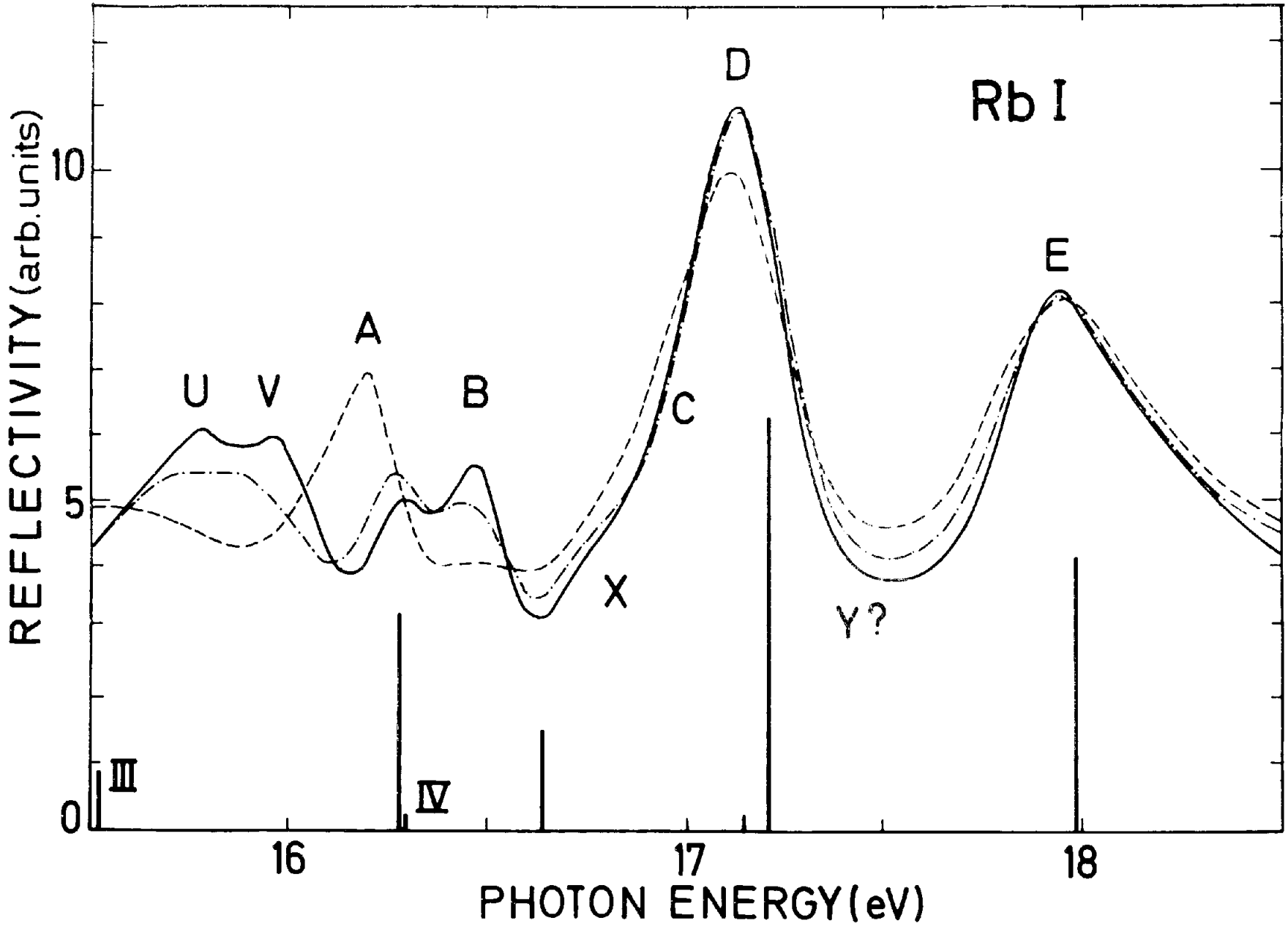
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PHOTON ENERGY (eV)