DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY

DESY SR-79/14
July 1979

# $K^+$3P-CORE EXCITONS IN POTASSIUM HALIDES STUDIED AT LOW TEMPERATURES WITH HIGH RESOLUTION

by

G. Sprüssel and M. Skibowski

*Institut für Experimentalphysik der Universität Kiel*

V. Saile

*Deutsches Elektronen-Synchotron DESY, Hamburg*

NOTKESTRASSE 85 · 2 HAMBURG 52

# K$^+$3P-CORE EXCITONS IN POTASSIUM HALIDES STUDIED AT LOW TEMPERATURES WITH HIGH RESOLUTION [++]

G.SPRÜSSEL AND M.SKIBOWSKI
INSTITUT FÜR EXPERIMENTALPHYSIK,UNIVERSITÄT KIEL
23oo KIEL 1,FEDERAL REPUBLIC OF GERMANY

V.SAILE
DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY
2ooo HAMBURG 5o,FEDERAL REPUBLIC OF GERMANY

## ABSTRACT

Reflection spectra of KF,KCl,KBr and KI single crystals have been measured at photon energies of approximately 2o eV with a bandwidth of 1o meV using synchrotron radiation in order to study fine structure and temperature dependence of the excitonic transitions associated with the K$^+$ 3p core level. The crystals were cleaved under ultrahigh vacuum and cooled down to 2oK. Information on energy positions, halfwidths and line shapes for the K$^+$3p-core excitons and their temperature dependence has been obtained. A new exciton predicted by the ligand field model was observed. For KI we evaluate an electron-hole exchange energy of only 3o(±7) meV.

---

[++] to be submitted to Solid State Communications

Absorption and reflection spectra for alkali-halides exhibit a series of prominent peaks in the UV and vacuum-UV which are associated with excitons from valence bands or deeper electron shells. Two approaches have been proposed to understand the specific features of these spectra: The excitons were either attributed to critical points in a band structure model (1,2,3,4) or more recently they were interpreted as ionic transitions in a ligand field model (5,6). Previous reflection and transmission experiments (2,3,4) have been performed on potassium halides in the region of the K$^+$3p excitation with rather limited spectral resolution in the range of the observed line widths (1oo-2oo meV), some of them under poor experimental conditions with regard to sample preparation. For a test of the theoretical predictions more accurate experimental information on energy positions, line profiles, halfwidths and their temperature dependence was desirable.

We therefore measured the reflectance for KF,KCl,KBr and KI around 2o eV at an angle of incidence of 15deg. We used the 3m-monochromator for synchrotron radiation from the storage ring DORIS (7) with a resolution of 1o meV. This bandwidth is by an order of magnitude smaller than that in previous measurements and was finally found to be well below the observed line widths. The potassium halide single crystals were cleaved under ultrahigh vacuum in a helium flow cryostat at low temperatures. The temperature at the surfaces of the samples was varied between approximately 2o K and room temperature (RT). It was monitored with a thermocouple calibrated by the sublimation point of condensed films of various rare gases .

Fig.1 shows the reflectivities for the four potassium halides in the region of approximately 2o eV at RT (dashed line) and at low temperatures (solid line). For all compounds we observe three strong and sharp peaks (A1,A2,C) and a shoulder (B) below peak C. The energy positions depend only weakly on the halide ions indicating that these transitions are localized at the potassium ion. Furthermore the first two coincide within o.4 eV with the 3p-core excitations of the free potassium ion K (8). For the free ion the ionization limit is split by 269 meV due to spin-orbit interaction while the first two transitions (3p to 4s and 3p to 4s') are separated by 4oo meV (8). For solid potassium halides we observe for the corresponding transitions 297(±2) meV for KF, 21o(±5) meV for KCl, 238(±4) meV for KBr, and 26o(±2) meV for KI.

The bars at the bottom of Fig.1 present the transitions predicted by the ligand field model. They are attributed to $p^6 \to p^5 s$ (A1,A2) and $p^6 \to p^5 d\gamma$ (V,B,C) transitions (5). As the ligand field model yields only energy differences and splittings, the absolute energy of the multiplet has been adjusted to the absorption measurements of Ejiri et al. (9). The heights of the lines give the relative oscillator strengths. In reflection we find only the four strongest transitions (A1,A2,B,C). Experiment and theory agree fairly well. Structures assigned to p,s- and p,d-transitions shift in the opposite direction with varying temperatures. The halfwidth of the d-peak C changes much more with temperature than that of the s-peaks. Sign and magnitude of thermal shifts are in rough agreement with the previously measured values for potassium halides at two temperatures (4,9,1o). The accuracy of our energy positions is better by a factor of about 1o.

For valence to conduction band transitions a thermal shift between RT and 7oK of about o.2-o.3 eV has been observed (11). In the case of the $K^+$3p core we find only approx. o.1 eV. From these different shifts we are able to distinguish between valence and core excitations. This leads us to assign the two peaks between 19 and 2o eV in KCl to valence and the following four structures to core excitations.

In detail we will discuss the case of KI. To compare our results with theory we calculate the imaginary part of the dielectric constant (EPS2) by a Kramers-Kronig-transformation (KKA) (12) using appropriate extrapolation procedures (see Fig. 2). The extremely high signal to noise ratio allows the calculation of the second numerical derivative of the spectra as shown in Fig.2. As can be seen in Fig.2 the relative intensities in reflectivity and EPS2-spectra differ. In EPS2 the oscillator strength of peak A1 is about a factor of 2 higher than that of peak A2 in contradiction to the predictions of the ligand field model (5) (see Fig.1) and previous measurements (9,1o). In order to evaluate accurate intensity ratios, the EPS2-spectra have been fitted with Lorentzians. This fit is in very good agreement with the experimental spectra when transformed into reflectivity. For all compounds - especially in the case of KI - the splitting of these two peaks is close to the spin-orbit splitting of the ionization limit of the free $K^+$3p levels. From the splitting and intensity ratio we expect a very small contribution of the electron-hole exchange interaction (13). With the model of Onodera and Toyozawa (13), the same spin-orbit splitting of the $K^+$ 3p levels in KI as in the free ion and the observed splitting of the first two transitions, we evaluate an electron-hole exchange interaction of 3o(±7) meV and an intensity ratio of 1.6(±o.1):1 for the peaks A1:A2. This value is identical with the result from our fit of EPS2.

It is important to note here that in the very sensitive second derivative spectra (see Fig.2) we find a new fifth structure with small oscillator strength at approximately 2o.5 eV. It shows the same temperature behavior as the other p,d-structures B and C. This is in excellent agreement with the predictions of the ligand field model (5) with two p,s- and three p,dγ-transitions. Also the fit with Lorentzians require a fifth structure at that energy position.

Looking at the minima of the second derivative spectra we find the expected differences for the energy positions of the reflectivity and EPS2-structures but both spectra yield the same thermal shifts within experimental errors (see Table 1). So it is sufficient to discuss the temperature dependence for the reflection spectra only. Fig.3 shows the temperature dependence of the peaks for KI derived from the minima of the second derivative reflection spectra (SDR). The error bars indicate experimental uncertainty for energy position and temperature. We interpolate the data points by a straight line although we expect a ctgh-like behavior at low temperatures.

The averaged temperature coefficient for the p,s-transitions is -o.29(±o.o2) meV/K and for the p,d-transitions +o.24(±o.o5) meV/K. The interpretation of magnitude and sign of the thermal shifts is complicated. Generally the temperature shift results from two terms: Lattice-expansion (L) and electron-phonon-interaction (P) (14).

In a simple local picture we may treat the shifts in the point charge model for ionic crystals (15). Then the L-term is the difference of the Madelung potential of the initial and the final states varying with temperature. The shift due to the Madelung potential has the same magnitude but opposite sign for anion and cation. For the anion this value is negative and for the cation positive with increasing temperature. In the case of the valence to conduction band transitions this L-term is negative since these excitations are regarded as charge-transfer transitions (15) from anion to cation. For this case, a ratio of approximately 2:1 was found for the contribution of the P- and L-term (11). For the lowest valence exciton at Γ a P-contribution of approx. -o.75 meV/K and a L-contribution of approx. -o.3o meV/K has been determined (see Fig.5, ref.11). In the case of the $K^+$3p-core excitations initial and final states are localized at the same ion. In this picture the L-term vanishes. Therefore the experimental shift is attributable to the P-term only. If this is true the different sign of the temperature coefficients for p,s- and p,d-transitions results only from different electron-phonon coupling in s- and d-final states.

A more sophisticated local approach is the ligand field model (5). From this model we may estimate the L-contribution as follows: The term energies and splittings of ionic transitions in the field of the nearest neighbors were calculated as a function of the crystal field parameter. The crystal field parameter varies with temperature because of the changing lattice constant. Then from the calculated term energy vs. crystal field parameter diagram (see Fig.1, ref 5) we expect only negative shifts and these shifts should be stronger for p,d- (approx. -o.o8 meV/K) than for p,s-transitions (approx. -o.o1 meV/K). This estimate for the L-contribution does not explain sign and magnitude of the observed temperature coefficient for the p,d-transitions. Combining the above estimated contribution due to lattice expansion with the experimental shifts we can derive a P-contribution of -o.28 (± o.o5) meV/K for the p,s- and +o.32(± o.o6) meV/K for the p,d-transitions. Again, the electron-phonon coupling apparently differs for the s- and d-final states.

## REFERENCES

1 J.C.PHILLIPS, Phys. Rev. **136**, A1721 (1964)

and: Phys. Rev. Letters **12**,142 (1964)

2 K.TEEGARDEN and G.BALDINI, Phys. Rev. **155**,896 (1966)

3 G.STEPHAN and S.ROBIN, Sol. State Commun. **5**,883 (1967)

and: C.R.Acad.Sci (France) **267**,4o8 (1968)

and: Optics Commun. **1**,4o (1969)

G.STEPHAN, E.GARIGNON and S.ROBIN, C.R.Acad.Sci (France) **268**,4o8 (1969)

4 D.BLECHSCHMIDT,R.KLUCKER and M.SKIBOWSKI
Phys.Stat.Sol. **36**,625 (1969)

D.BLECHSCHMIDT,R.HAENSEL,E.E.KOCH,U.NIELSEN and M.SKIBOWSKI
Phys.Stat.Sol. (b) **44**,787 (1971)

5 C.SATOKO, Sol. State Commun. **13**,1851 (1973)

C.SATOKO, and S.SUGANO, J. Phys. Soc. Japan **34**,7o1 (1973)

6 V.SAILE,N.SCHWENTNER,M.SKIBOWSKI,W.STEINMANN and W.ZIERAU
Phys.Letters **46A**,245 (1973)

W.ZIERAU and M.SKIBOWSKI,J.Phys.C **8**,1671 (1975)

7 V.SAILE,P.GÜRTLER,E.E.KOCH,A.KOZEVNIKOV,M.SKIBOWSKI and W.STEINMANN, Appl.Opt. **15**,2559 (1976)

8 C.E.MOORE, Atomic Energy Level,
Circ.Nat.Bur.Standards 467 (1949)

9 A.EJIRI,M.WATANABE,H.SAITO,H.YAMASHITA,T.SIBAGUCHI,H.NISHIDA and S.SATO
Proceedings of the 3rd Int.Conf. on VUV Rad.Phys. Tokyo
1pB1 (1971)

1o H.SAITO, Science of Light **2o**,no.1 (1971)

11 T.TOMIKI,T.MIYATA and H.TSUKAMOTO, Z. Naturforsch. **29a**,145 (1974)

12 R.KLUCKER and U.NIELSEN, Computer Phys.Commun. **6**,187 (1973)

H.J.HAGEMANN,R.KLUCKER and U.NIELSEN, Internal Report DESY-F41-73/1o (1973)

13 Y.ONODERA and Y.TOYOZAWA, J.Pys.Soc.Japan **22**,833 (1967)

14 K.BAUMANN, Phys.Stat.Solidi (1) **63**, K71 (1974)

P.B.ALLEN and V.HEINE, J.Phys.C **9**,23o5 (1976)
and references therein

15 P.H.CITRIN and T.D.THOMAS, J.Chem.Phys. **57**,4446 (1972)

Table 1

Energy positions for KI at RT and 2oK from the SDR- and the EPS2-data together with the total shift. All values are given in eV.

| | | A1 | A2 | V | B | C |
|---|---|---|---|---|---|---|
| SDR | RT | 19.946 | 2o.2o2 | 2o.62 | 2o.77 | 21.1o8 |
| | 2oK | 2o.o21 | 2o.284 | 2o.55 | 2o.72 | 21.o36 |
| | uncertainty | ±.o1o | ±.o1o | ±.o9 | ±.o4 | ±.o1o |
| | total shift | -o.o75<br>±.oo5 | -o.o82<br>±.oo5 | +o.o7<br>±.o4 | +o.o5<br>±.o2 | +o.o72<br>±.oo5 |
| EPS2 | RT | 19.93 | 2o.17 | 2o.65 | 2o.77 | 21.o3 |
| | 2oK | 2o.o1 | 2o.26 | 2o.54 | 2o.71 | 2o.99 |
| | uncertainty | ±.o2 | ±.o2 | ±.1o | ±.o8 | ±.o3 |
| | total shift | -o.o7<br>±.o1 | -o.o9<br>±.o1 | +o.11<br>±.o6 | +o.o7<br>±.o5 | +o.o5<br>±.o2 |

## FIGURE CAPTIONS

Fig.1 Reflectivity spectra of the potassium halide single crystals at room temperature (RT) (dashed line) and the lowest temperature (solid line) together with the predictions of the ligand field model (vertical bars at bottom)

Fig.2 Reflectivity spectra and the imaginary part of the dielectric constant (EPS2) for KI at the two extreme temperatures together with the second numerical derivative

Fig.3 Temperature dependence of the energy positions for the five excitations A1,A2,V,B and C in KI. The straight lines represent least-square fits. For V the experimental points (which scatter more, see Table 1) are not included.

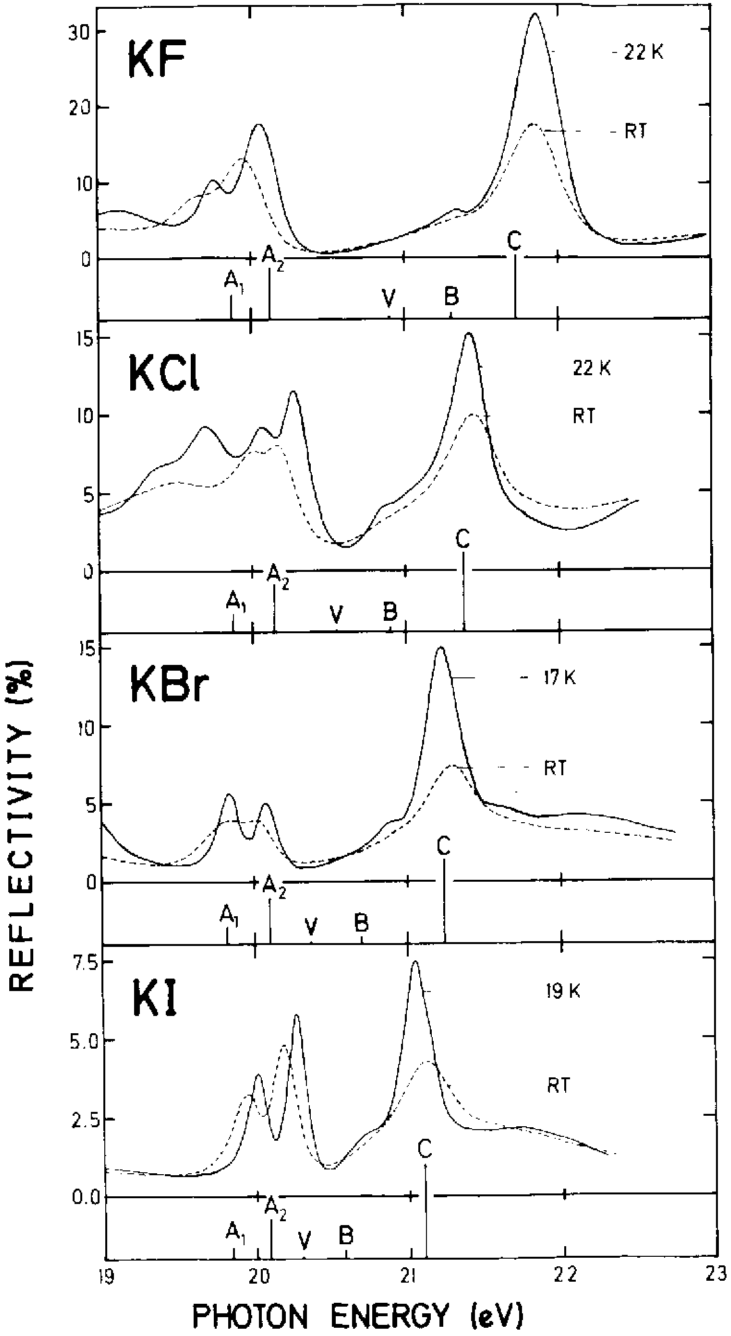

Fig. 1

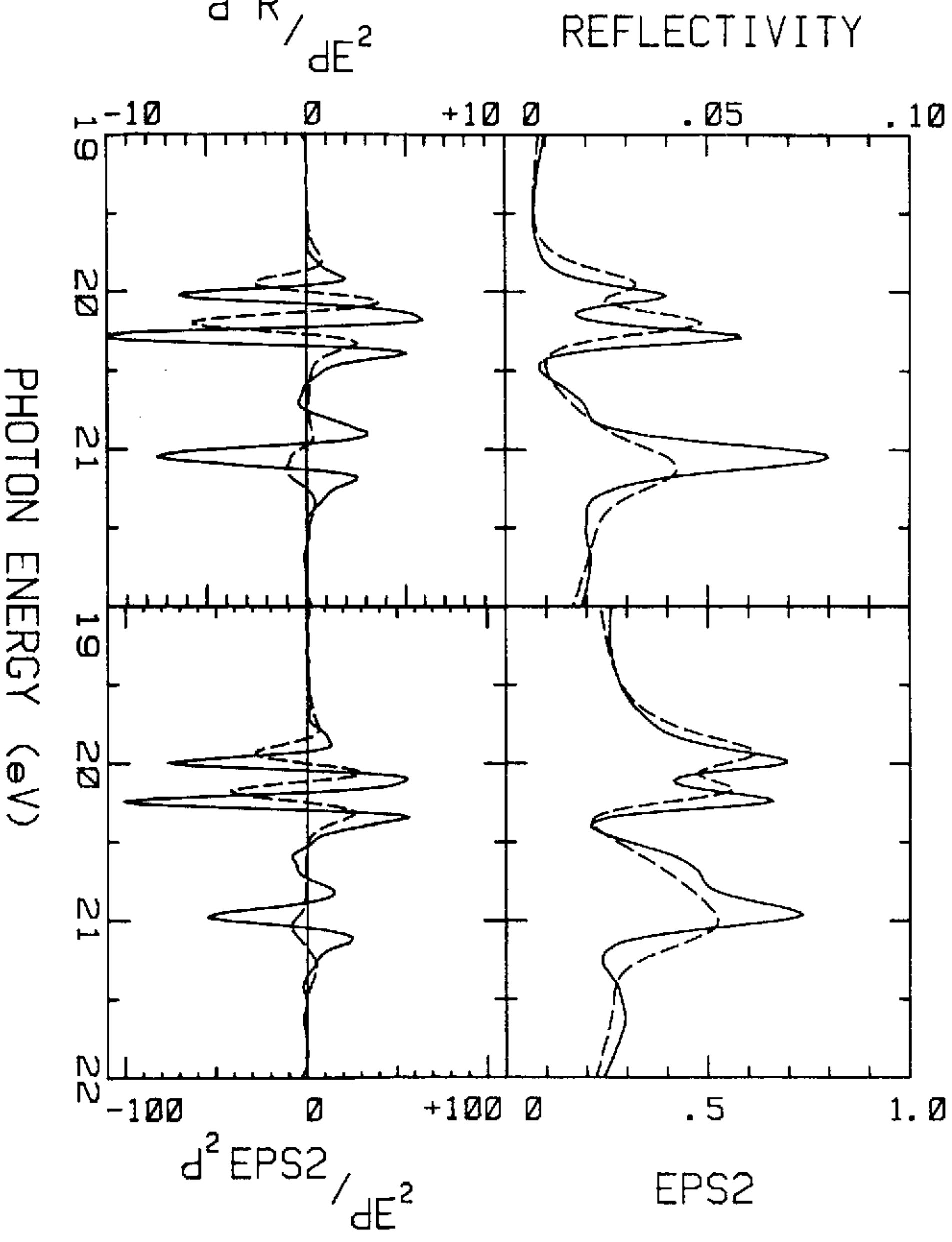
d²R/dE²
REFLECTIVITY
-10
0
+10
0
.05
.10
19
20
21
22
PHOTON ENERGY (eV)
-100
0
+100
0
.5
1.0
d²EPS2/dE²
EPS2

Fig. 2

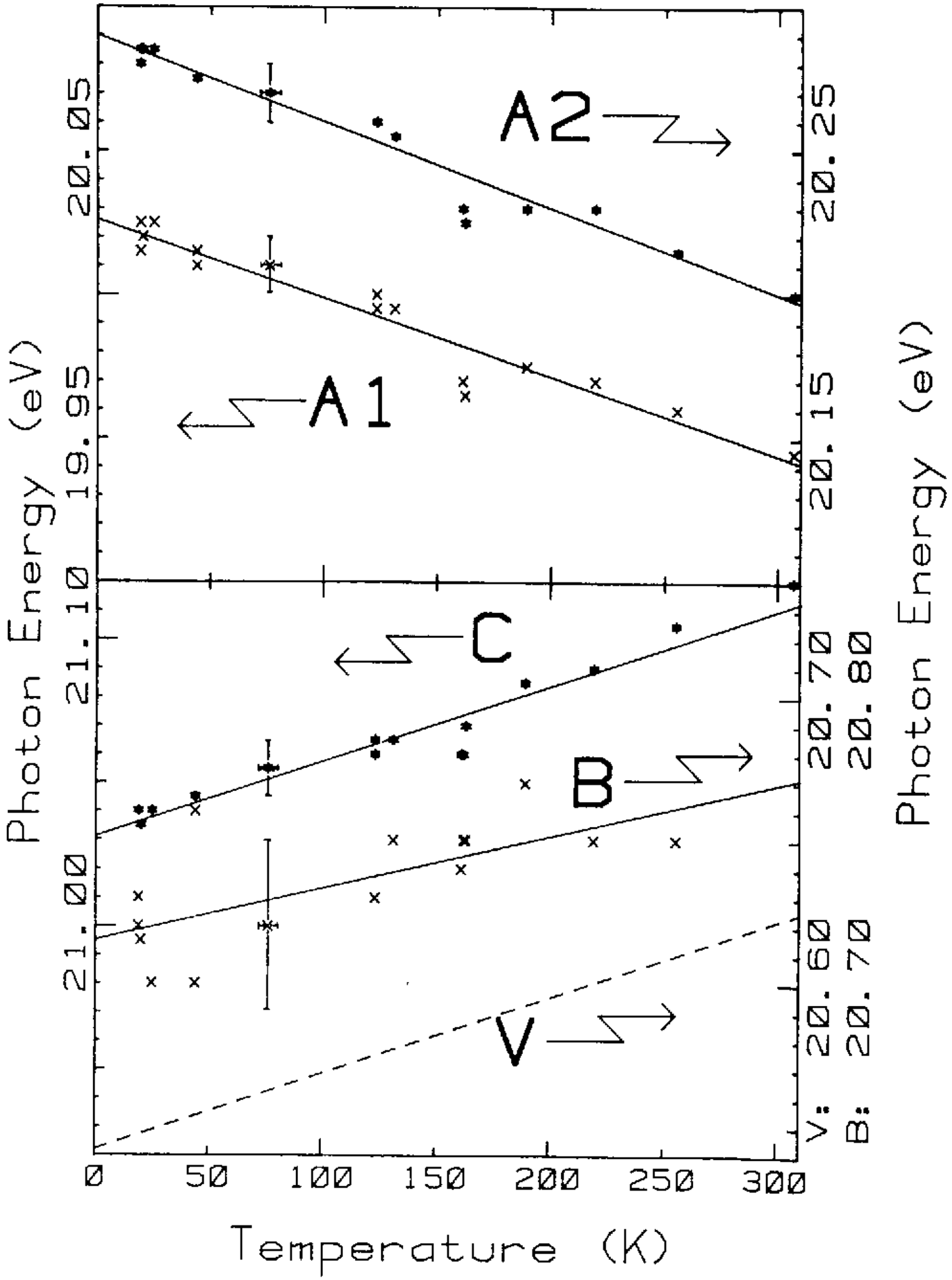
A2
A1
C
B
V
Photon Energy (eV)
20.05
19.95
21.10
21.00
20.25
20.15
20.70
20.80
20.60
20.70
V:
B:
Photon Energy (eV)
0
50
100
150
200
250
300
Temperature (K)

Fig. 3