

FIG. 1. Log-log plot of the direct relaxation rate coefficient A as a function of the Zeeman field H . The line drawn through the experimental data points represents a fourth-power field dependence as predicted by Van Vleck's theory

stantial uncertainty. These points, although consistent with the more precise values measured at lower temperatures, were therefore omitted from the graph.

It is seen that the data are satisfied by the

function

$$1/T_1 = cH^n T + 4.3 \times 10^{-3} T^9 \text{ (sec}^{-1}\text{)},$$

with $3.88 \leq n \leq 4.06$ and where c is a proportionality constant. We believe this to be the first confirmation of the Van Vleck field dependence for a case in which his theory should clearly apply.

It is perhaps useful to point out that if the mechanism is correct, then the field dependence relies only on the assumptions that (1) the density of phonon states is quadratic in energy at energies well below the Debye value, (2) the strain produced by long-wavelength phonons is proportional to the square root of the frequency, (3) phonons obey Bose statistics, and (4) the matrix elements of vibrating crystal potential vanish between Kramers conjugate states. A departure from any of these assumptions would be rather difficult to understand.

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INTERBAND EXCITON AND SCATTERING STRUCTURE IN THE ULTRAVIOLET SPECTRA OF ALKALI HALIDES AND SOLID RARE GASES*

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We have completed a quantitative, categorical analysis of the uv spectra of the alkali halides^{1,2} and solid rare gases³ similar to that previously carried out for semiconductors.⁴ The results are unusually rich in detail, inasmuch as more than 30 new Van Hove edges in the scattering spectra and 17 new metastable excitons have been

identified and analyzed with regard to line shape and intensity. In this Letter we set forth the physical ideas which have emerged from our detailed analysis.

(1) On the basis of physical arguments concerning the effective potential^{5,6} seen by valence and conduction electrons, we have been able semi-

empirically to deduce the energy band structure of these crystals over a range of 15 eV from Van Hove interband scattering edges in the uv data. The results for KI, together with the principal interband transitions used to obtain them, are shown in Fig. 1. In Table I some important transitions are classified for KI and KBr.

(2) The energy bands so constructed provide a natural explanation for the plateau in the photoemission of the alkali halides above threshold which has puzzled previous workers.² With the vacuum level marked in Fig. 1, it is apparent that there is a range of direct thresholds from 7.5 eV along the (111) axis to 8.5 eV along the (100) axis. Above the 8.5-eV threshold all photoelectrons will be able to escape with equal probability.

(3) Having interpreted the interband scattering spectra, we were in a position to analyze the exciton spectra which have puzzled previous workers.^{7,8} Of course, the first two large exciton peaks are conventionally (and correctly) associated with 1s electron-hole bound states,⁹ the electron wave packet being made up of states near Γ_1 and the hole wave packets from the spin-orbit split levels $\Gamma_{15}(J=3/2)$ and $\Gamma_{15}(J=1/2)$. The puzzle has revolved around the "extra" exciton states which are shown in Fig. 2 for KI. We have positively identified these as metastable excitons.¹⁰

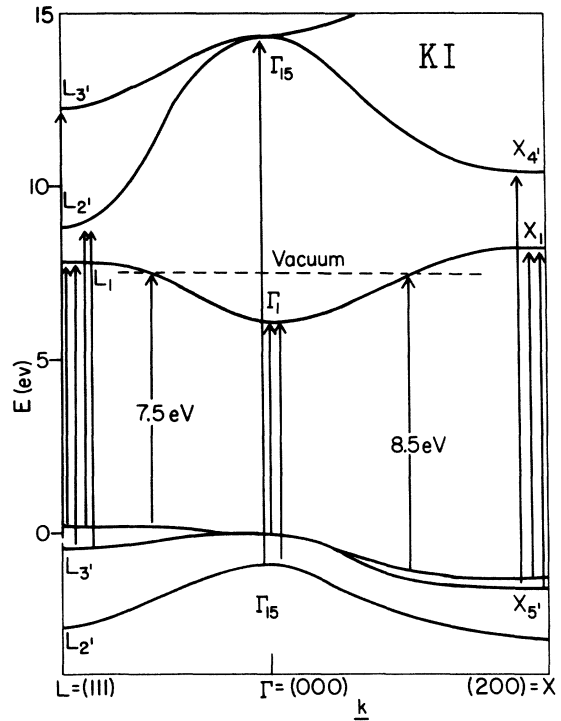


FIG. 1. The energy bands of KI along the principal symmetry directions ΓL and ΓX as deduced semiempirically. The principal interband transitions that have been identified at Γ , X , and L are marked. The direct interband photoemission thresholds to vacuum level in the (111) and (100) directions are marked also.

Table I. Interband scattering and exciton edges in KI, KBr. Interband edges of type M_1 are strong (S) or weak (W). Edges of type M_0 are proportional to $(E - E_0)^n$, where $n = 1/2$ or $3/2$ as indicated, for allowed or forbidden thresholds. The binding energy of an exciton is measured from the parent interband edge. The single group representations at $\Gamma(L)$ are labeled by $J(m_j)$ values to include the effects of spin-orbit splitting.

KI, KBr Scattering edges	Van Hove type	Strength (n)	Energy	
$\Gamma_{15}(3/2) \rightarrow \Gamma_1$	M_0, M_0	S, S	6.1, 7.8	
$\Gamma_{15}(1/2) \rightarrow \Gamma_1$	M_0, M_0	S, S	7.0, 8.3	
$L_{3'}(3/2) \rightarrow L_1$	M_1, M_0	S, 1/2	7.7, 10.6	
$L_{3'}(1/2) \rightarrow L_1$	M_1, M_0	S, 1/2	8.3, 10.9	
$L_{3'}(3/2) \rightarrow L_{2'}$	M_0, M_1	3/2, W	8.7, 9.5	
$L_{3'}(1/2) \rightarrow L_{2'}$	M_0, M_1	3/2, W	9.3, 9.8	
$X_{5'} \rightarrow X_1$	M_1, M_1	S, S	[9.3, 9.6], 11.5	
$X_{5'} \rightarrow X_{4'}$	M_1, M_1	W, W	11.5, 13.3	
Excitons (metastable)		Energy (eV)	Binding energy (eV)	
		$\Gamma(3/2)$	5.80, 6.77	0.4, 1.0
		$\Gamma(1/2)$	6.68, 7.26	0.3, 1.0
		$L(3/2)$	6.88, 8.6	0.9, 2.0
		$L(1/2)$	7.25, 8.9	

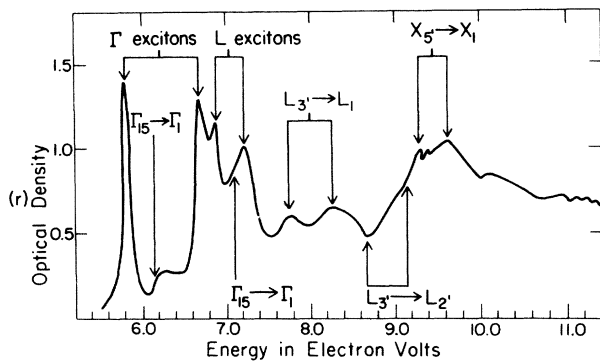


FIG. 2. The ultraviolet spectrum of KI in the exciton and low interband region at 80°K (see reference 1). The important interband edges and excitons are labeled (see also Table I).

In fcc lattices the electron wave packet is made up out of states near L_1 or L_2' and the hole wave packet is made up out of states near L_3' . The metastable excitons are denoted by "L excitons" in Fig. 2. Their characteristic properties are the following:

(a) Their binding energy is two to four times the binding energy of Γ excitons. This is a result of the much larger volume of momentum space¹⁰ available to L excitons. Note that metastable L excitons have previously been hypothesized to explain line narrowing¹¹ and hyperfine structure in semiconductors.¹⁰ The metastable excitons introduced here have binding energies of order 1 eV, whereas in semiconductors the binding energy is at most 0.1 eV (less than linewidth).

(b) In fcc lattices the spin-orbit splitting is characteristic of the valence p levels at L, not Γ . For the alkali halides this yields a splitting about half that of Γ excitons. For Xe the valence-band width is so small that L_3' and L_2' are quasi-degenerate and the splitting of the L excitons (10.30, 11.15 eV) is 3/4 that of the Γ excitons (8.36, 9.53 eV).

(c) In bcc lattices the metastable exciton is derived from the nondegenerate valence- (conduction-) band edges N_4' (N_1). One extra exciton peak is predicted and one is observed in CsCl, Br, and I.

(d) Of great theoretical interest is the change in shape of the direct absorption threshold in the alkali halides (identified by Taft and Philipp¹²) on passing to Xe. It is shown that the over-all electronic band shape of the alkali halides and the solid rare gases is quite similar. The unusual

step characteristic of the direct absorption threshold has been explained qualitatively as a polaron effect by Dexter.¹³ Because Xe is monatomic, one obtains in annealed specimens a normal line shape for the threshold, with the polaron self-energy "turned off." By not annealing the specimen, Baldini obtains³ an absorption shoulder in Xe of the same shape as in the alkali halides. The polaron effect is "turned on" by lattice defects, in agreement with Dexter's qualitative arguments. It is evident that the optical spectra of these crystals demonstrate interesting many-body effects.

(e) In the bromides and chlorides, when the alkali atom is K or Rb, metastable L excitons are present with a linewidth comparable to that of the first (stable) Γ exciton. The Li and Na salts exhibit no metastable excitons. In the interband spectrum the M_1 Van Hove edges $L_3' \rightarrow L_1$ are broad when metastable excitons are present, whereas in LiBr with no metastable excitons edges of nearly ideal shape are resolved¹ at 9.3 and 10.7 eV.

The metastable excitons overlap the continuum of interband scattering transitions and it is difficult to understand their long lifetime. This puzzle can be resolved by assuming that metastable excitons consist of an electron in the conduction band bound to a self-trapped hole. It has been shown by Castner and Känzig¹⁴ that the Jahn-Teller effect can self-trap holes in the alkali halides. The hole is bound to a halogen₂⁻ molecule.

Of course, because the exciton is neutral, the polaron self-trapping energy of an exciton is much smaller than that of a hole. Thus for the small alkali atoms (large halogen-halogen overlap) the mobility in the valence band is large enough to prevent self-trapping. For the large alkali atoms (smaller halogen-halogen overlap) self-trapping occurs. This explains self-trapping for K and Rb but not for Li and Na. Finally, the distortion of the lattice by the Jahn-Teller effect may occur (to a lesser extent) for scattering states as well,¹⁰ explaining why the $L_3' \rightarrow L_1$ edge is broad when metastable excitons are present, sharp when they are absent. It may be that the breadth of $L_3' \rightarrow L_1$ edges is a lifetime effect caused by nonradiative decay to metastable excitons.

If the long lifetime of the metastable exciton is due to self-trapping on a diatomic molecular ion, then we are dealing with breakdown of the Franck-Condon principle. (Such breakdown is not un-

known in molecular spectra.¹⁵) For Xe the energy gain due to molecular formation in the excited state has been estimated by Mulliken¹⁶ to be 0.5 to 1.0 eV. The total binding energy of the metastable exciton in Xe, measured relative to its parent interband edges, is about 1.5 eV. It appears that about half the binding energy can be ascribed to Jahn-Teller formation of the molecular ion.

A complete analysis of the spectra^{1,2} for Na, K, Rb, and Cs compounded with Cl, Br, and I as well as the spectra of Kr and Xe³ will be given elsewhere.¹⁷ I am grateful to S. Rice, M. H. Cohen, and R. Mulliken for stimulating discussions of the self-trapped exciton.

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RESISTIVE TRANSITIONS AND SURFACE EFFECTS IN TYPE-II SUPERCONDUCTORS

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We have been using sheet samples of type-II superconductors to investigate resistive transitions in the mixed state. When the external magnetic field is applied parallel to the sample surface, superconductivity in these materials persists far beyond Abrikosov's upper critical field H_{C2} . Recently, Saint-James and de Gennes¹ have shown by solving the Gor'kov-Landau equations with physical boundary conditions, that in parallel fields nucleation to a superconducting sheath will occur at the field $H_{C3} = 1.695H_{C2}$. In this Letter we report our experimental results relevant to this theoretical calculation.

Measurements of longitudinal voltages (along the direction of J) on a well-annealed Nb-Ta sample are shown in Fig. 1. The external field H is provided by a Varian magnet rotatable around the vertical axis. When H is aligned parallel to the sample surface, a sharp transition takes place at $H = H_{C2}$, but partial superconductivity persists far beyond H_{C2} .² The angular dependence of the

resistance is so sensitive that the $\theta = 0$ orientation is usually determined by measuring voltages as a function of θ with H set slightly above H_{C2} . For this particular sample orientation, J is parallel to the rolling direction (RD) of the sample and H becomes parallel to J at $\theta = 0$. Measurements have been made for $J \perp \text{RD}$ and/or $J \perp H$ at $\theta = 0$ to establish that the observed phenomenon is essentially a surface effect. Because of this, the resistance above H_{C2} depends strongly on the measuring currents, as is shown by plotting R/R_N for various currents at the $\theta = 0$ orientation. As the current is decreased, the spike at H_{C2} diminishes in height and the return to the normal resistivity takes place more gradually. This behavior is very similar to the remanent superconductivity observed in Ta wires (type-I superconductor) by Seraphim and Connell³ and by Budnick.⁴ The residual superconductivity beyond H_{C2} has been observed in Nb wires by Autler, Rosenblum, and Goen⁵ and in Pb-In wires by Druyvesteyn,