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I. INTRODUCTION

This quarter saw the conclusion of the alkali halide work of Thomas H. DiStefano. His thesis has been written and copies will be available for distribution within a month or two. The abstract of this thesis is included as Part III of this report.

Robert S. Bauer has completed photoemission measurements on the silver halides. Part II of this report is based on new experimental data and a theoretical investigation of the very large temperature effects found in the silver halides. Experimental methods were devised so that temperature could be varied continuously between room and liquid nitrogen temperatures. As a result, more detailed information on the temperature dependence has been obtained. This detailed information is found to be in agreement with the theoretical models presented in Part II.

In addition to the work reported in Parts II and III, preliminary work has been done in two new areas: (1) Estimates of photoemission from the surface of the moon and (2) development of photoemission to serve as standard absolute detectors in the ultraviolet.

II. Giant Temperature Dependence of Photoemission from the Silver Halides

R. S. Bauer

ABSTRACT: Anomalous temperature dependent photoemission has been measured from the silver halides. Structure in the photoemitted electron energy distributions sharpens dramatically as samples are cooled from 295^oK to 80^oK. We believe this is due to a lattice vibrationally dependent p-d hybridization of the valence states. Using this effect, we have experimentally located the Ag states with almost pure 4d symmetry at 3.6 eV and 3.3 eV below the highest valence states in AgBr and AgCl respectively.

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The characteristics of the electronic states of the silver halides are profoundly influenced by the proximity in energy of the Ag 4d electron states to the halogen p states. In fact, the mixing of these wave functions is so large that the hybridized states near L are increased in energy by a few eV relative to the Γ levels thereby creating a maximum in the valence band in the L direction.¹ We have observed (see Figs. 1 and 2) unusually large and dramatic changes in the energy distribution curves (EDCs) of electrons photoemitted from the silver halides upon cooling from 295^oK to 80^oK.² The optical properties also exhibit striking, but less well-defined, changes upon temperature variation.^{3,4} We find that these changes occur because of dynamic variations in the electronic states

due to the dependence of the large p-d mixing on the vibrations of the lattice. At room temperature, where the amplitude of the lattice vibration is large, the energy levels are broadened by as much as 1 eV by the fluctuating p-d overlap. At liquid nitrogen (LN_2) temperature, where the amplitude of ionic vibrations is small, the hybridized levels become sharper and more well defined. We thus associate the observed changes with a temperature dependent dynamic hybridization of the electronic states.

The samples studied were epitaxial, thin films evaporated onto vacuum heat-cleaned silver at less than 3×10^{-8} Torr from 99.999% pure AgBr and AgCl powder. The films were about 200\AA thick to eliminate charging at low temperatures. At room temperature, the photoemissive properties of these thin films were essentially identical to those of films 0.6μ thick. Electron microscopy⁵ and optical^{4,6} studies have established that evaporated thin films are good model systems for bulk silver halide properties. Photoemission from these samples was measured in situ at less than 5×10^{-11} Torr using the standard ac method⁷ for photon energies, $h\nu$, through 11.8 eV. New techniques were developed to measure photoemission at any temperature between room and liquid nitrogen values. By using forming gas and helium in a liquid nitrogen heat exchanger, the sample temperature could be set and maintained to within $\pm 4^\circ\text{K}$. The experimental results were reproducible following temperature cycling and among different samples.

The most striking feature of the EDCs in the 10 eV photon energy range (see Fig. 1) is the sharpening of the structure with reduced temperature. For example, in AgBr, the full width of the central peak

at 90% of its maximum height decreases from about 0.7 eV to 0.3 eV upon cooling from 287°K to 80°K. In both materials, room temperature shoulders are resolved into well-defined peaks at 80°K. At higher photon energies (see Fig. 2), a strong new peak appears in AgBr at 80°K which is not present at room temperature. As seen in Fig. 1, these changes occur gradually as the temperature is varied.

These changes upon cooling are an order of magnitude larger in the silver halides than the changes in photoemission from most materials. In a wide variety of other solids, the changes in the photoemission EDCs upon temperature reduction are very small (comparable to the change in kT) and for the most part can be explained simply by absorption or emission of a small number of phonons.⁸ The energies involved in such events are much too small to cause the giant variations we observe in the silver halides. Therefore, the lattice must be greatly affecting the electronic states directly rather than simply through phonon absorption and emission by the photoexcited electron. We must thus examine the nature of the filled electronic levels to understand why this effect occurs in the silver halides but not in most other materials. As noted above, the overlap of the halogen p and Ag 4d wave functions has a large effect on the energies of the halogen p-derived states in the solid. Since this wave function overlap is dependent on the separations of the ions, the energies of the hybridized states will be affected by changes in this spacing. Thus, as the ions vibrate about their equilibrium lattice position, the dynamic changes in ionic separation will cause a considerable modulation

of the energies of the hybridized states. Such energy broadening will, of course, be temperature dependent, for as the temperature is lowered below the Debye temperature, Θ_D , the dynamical motion of the lattice is significantly reduced. This will result in smaller fluctuations of the hybridization with a corresponding reduction in broadening of the energy. Thus, we believe it is the thermal vibrations of the lattice which are affecting the electronic states. As will be shown, this effect is an order of magnitude larger than the energy shifts caused by the contraction of the lattice upon cooling.

To obtain a rough estimate of the magnitude of the dynamic hybridization effect, we made a tight-binding calculation^{9,10,11} of the AgCl valence band maximum, L_3' , as a function of lattice constant. Though not directly comparable to any measured EDC structure, the energy of this state provides an order of magnitude estimate for the experimental broadenings since its large hybridization¹² makes it particularly sensitive to ionic separation. From calculations made with an unscreened Slater exchange potential in the course of the work reported in Refs. 10 and 11, Fowler estimates that each of the two-center integrals changes by an average of about 5% upon a 1% change in lattice constant.¹³ We have calculated the rms displacement of the ions as a function of temperature using the Debye-Waller theory.¹⁴ Assuming an equal displacement for the two types of ions and one atom per unit cell with a mass which is the mean¹⁵ of the two constituents, the rms displacements are found to be about 0.26 Å at room temperature for both AgBr and AgCl. This is within 10% of the rms displacement of each ion in AgCl determined from neutron diffraction measurements.¹⁶ Using the calculated rms displacement to estimate maximum and minimum values

for the lattice constant, we calculate a variation in energy of the AgCl L_3' state of about 1.1 eV at room temperature. Because of the similarity of the band structures of AgCl and AgBr,^{11,17} we would expect the broadening of the AgBr valence band maximum to be of a comparable magnitude. Our simple calculation thus indicates that the lattice vibrational modulation of the overlap produces fluctuations in the energies of the hybridized states which is of the same magnitude as the observed broadening of the photoemission EDCs (e.g., 0.7 eV for AgBr at 287°K seen in Fig. 1).

Upon cooling to 80°K, the rms ionic displacement is reduced to 0.14Å resulting in a smaller calculated L_3' broadening of about 0.6 eV. This decrease of 0.5 eV in the dynamic variations of the AgCl L_3' energy is comparable to the 0.4 eV sharpening of the central AgBr EDC peak in Fig. 1. It is the changing amplitude of vibration of the ions which causes the temperature dependent broadening rather than the AgCl lattice contraction of 0.033Å¹⁸ since the contraction produces an L_3' shift of less than 0.1 eV upon cooling from 295°K to 80°K and, of course, no change in broadening. Thus, our rough calculations indicate not only that the dynamic fluctuations in the wave function overlap produce modulations of the electronic state energies comparable to the observed broadenings, but also that the changes of these energy variations upon temperature reduction are of the same order of magnitude as the measured EDC temperature dependences. In addition, since the broadening depends on the amplitude of the ionic vibration, the gradual dependence on temperature seen in our experiments (Fig. 1) is to be expected.

This temperature dependent dynamic hybridization causes the loss of well-defined structure in the absorption edge above approximately 15°K^{19,20}

(i.e., for $T > \text{approximately } 0.1 \Theta_D$). In addition, the large pressure dependence of the silver halide absorption edge²¹ is expected from the strong dependence of the hybridized state energy on ionic spacing in our model.

There is another way in which the dynamic broadening can be estimated from experimental data. The pressure dependence of the indirect band edge²¹ gives a measure of energy level vs equilibrium ionic separation. One can utilize this energy versus position data to estimate the dynamic broadening effects due to the rms displacement of the ions at elevated temperatures. Using the rms ionic displacement to compute an equivalent fractional volume change, a total energy variation of the valence band maximum at room temperature of about 0.9 eV in AgCl and 0.8 eV in AgBr is deduced due to the fluctuation in hybridization produced by the lattice vibrations. This broadening is comparable to both the calculated and experimental values presented above. Consistent with our other findings, it is reduced by over 0.3 eV for both halides upon cooling to 80°K. Thus, the predictions of our dynamic hybridization model for the magnitudes of both the dynamic broadenings and the changes upon cooling of these broadenings are quite comparable to the corresponding EDC magnitudes when computed either from purely theoretical considerations or by extension of other experimental results.

It is important to note that this model predicts that the amount of change of the photoemission EDCs upon temperature variation will depend on the amount of hybridization of the states from which the electrons are

photoexcited. This effect is, in fact, seen in the data. In the representative EDCs presented in Fig. 2 for AgBr, it is seen that only certain transitions sharpen drastically upon cooling the sample. The structure on the left side of this figure shows no significant changes upon temperature variation. Calculations show that the uppermost Ag 4d states produce very flat bands;^{11,17} this is usually indicative of states which are not significantly hybridized. Since the energy of such "pure" states does not depend on wave function overlap, one expects from our model that the energy of these states will not be greatly affected by the vibrations of the lattice. Hence the photoemission from these states will exhibit a much smaller temperature dependence than for the hybridized states. In fact, this smaller temperature dependence is comparable to that found in most materials.⁸ We thus associate the -3.6 eV peak in AgBr² (and similarly the -3.3 eV structure in AgCl²²) with the highest Ag 4d-derived states (all energies are referred to the valence band maximum). The temperature dependent transitions from initial states of 0 to -3.2 eV in AgBr and 0 to -3.0 eV in AgCl are believed to be from the more hybridized halogen p-derived levels. This -3.6 eV "pure" Ag 4d location in AgBr is precisely the energy determined for these states in high photon energy ($h\nu_{\max} = 26.8$ eV) room temperature studies we conducted.²³ In fact, these d locations in both silver halides agree remarkably well with the corresponding flat bands in the speculative electronic structures of Bassani, Knox, and Fowler.¹¹

Further credence for the dynamic hybridization is given by Green's function approach to this problem by Doniach.²⁴ This theory, which takes into account random variations in tight-binding overlaps induced by the ionic motion, predicts that structure in the density of hybridized states will not only vary in

width, but also will exhibit height changes and shifts upon cooling the solid. This formalism may explain some of the more complex features of the photoemission data which we have not discussed. Such features and the detailed dependence of the EDC broadening on temperature will be fully explored in future work on AgI as well as AgBr and AgCl.

The authors gratefully acknowledge stimulating and fruitful discussions with A. D. Baer, F. C. Brown, T. H. DiStefano, S. Doniach, W. B. Fowler and L. Sutton as well as other colleagues at Stanford University. We are particularly indebted to W. B. Fowler for providing the estimates for the affect of lattice constant variation on the tight-binding band parameters.

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Figure Captions

- Fig. 1 Comparison of energy distributions, N , normalized to quantum yield (per incident photon) for electrons photoemitted from AgBr ($\Theta_D \approx 144^\circ\text{K}$) and AgCl ($\Theta_D \approx 162^\circ\text{K}$) at 80°K through 287°K for photon energies of 10.2 eV and 10.4 eV respectively. (The electron energy is referred to the valence band maximum, E_v .) Caution should be taken in comparing the heights of the curves since they are normalized relative to the incident rather than the absorbed photon flux due to the lack of low temperature optical data in this photon energy range.
- Fig. 2 Comparison of energy distributions, N , normalized to quantum yield (per incident photon) for electrons photoemitted from AgBr at 80°K and 295°K for photon energies of 11.0 eV through 11.8 eV.

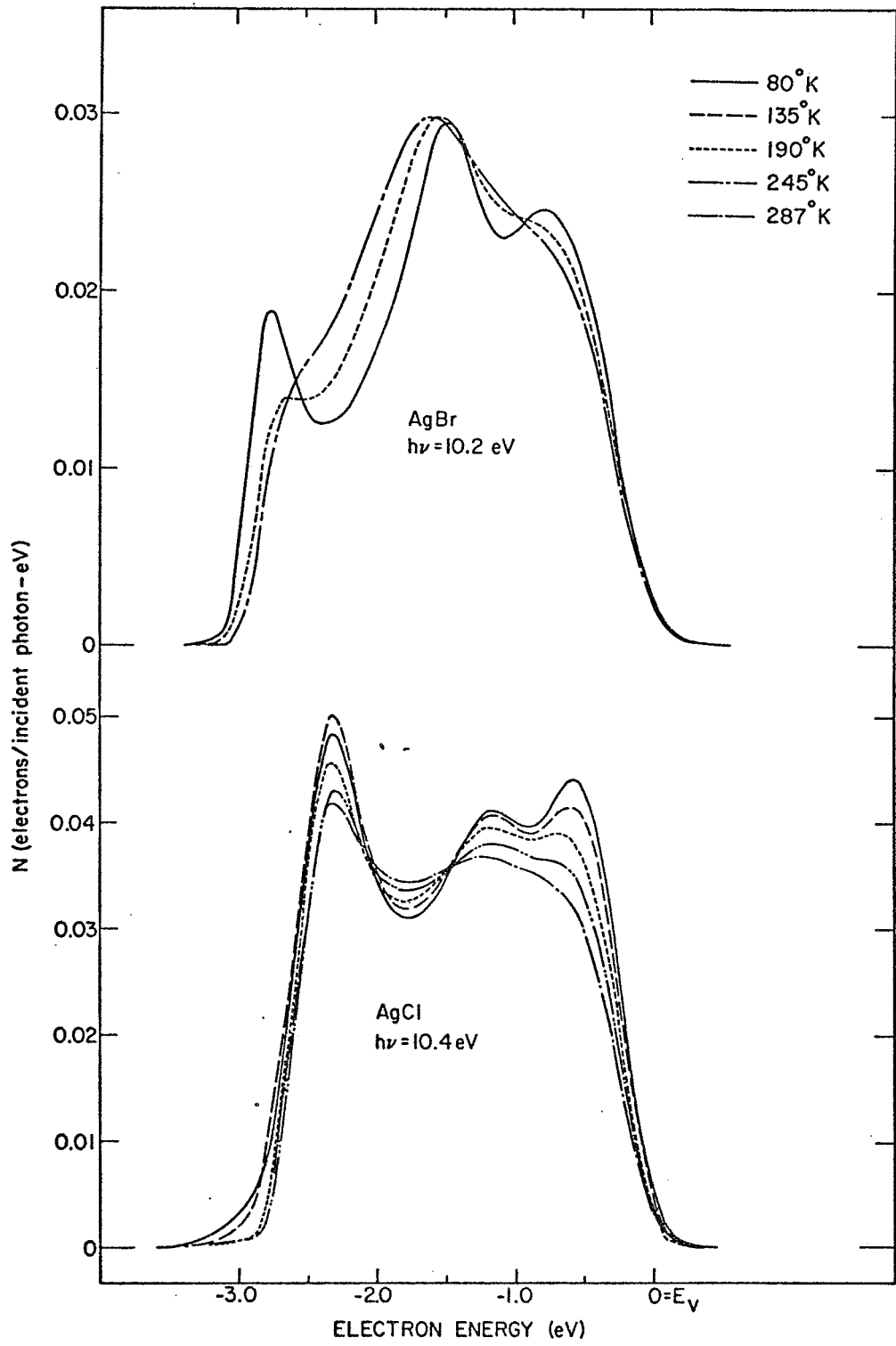


Figure 1

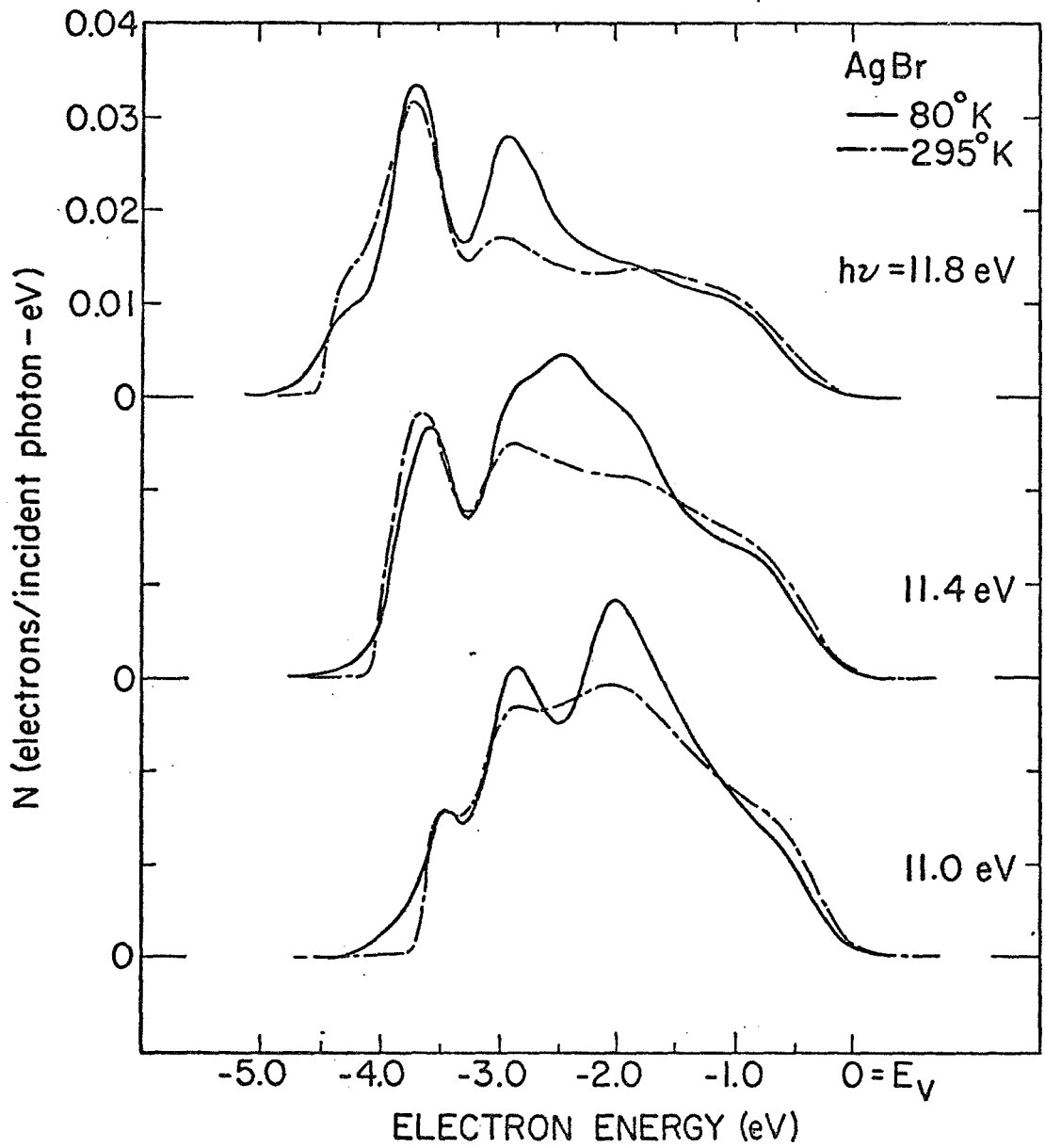


Figure 2

III. Photoemission and Optical Studies of Ionic Insulators

T. H. DiStefano

Photoemission measurements in the vacuum U.V. are reported for the alkali iodides, with some emphasis upon determining the general nature of ionic insulators. By a resolution of details in the photoelectron spectra from very thin films, information was obtained about the electronic states in both the valence and the conduction bands. Also, a technique of photoinjection was developed to determine scattering of hot electrons in wide gap insulators.

In narrow band materials, there is a possibility that electron-electron correlation will cause a localization of the electronic wavefunction. In Hartree-Fock terms, the Wannier state may lie at lower energy than the Bloch state. Intensive photoemission measurements on CsI shows evidence for Bloch valence states. Three salient peaks in photoemission from CsI are well explained in terms of optical excitation from three branches of the valence band dispersion curve. On the other hand, only a doublet could be produced by excitation from localized ionic levels. Calculated photoelectron spectra based upon interpolations of an existing band structure compare favorably with experiment. No concrete evidence for either Bloch or localized states was found in the fcc alkali iodides.

Trends in electron affinity, photoelectric threshold, and valence band width are found in the alkali iodides. The average spin-orbit splitting of the valence bands is seen to range from 0.95 eV to 1.6 eV. In all of these materials but RbI, narrow conduction bands were found in the first several eV above the band edge. These flat bands quite possibly comprise d-symmetry wavefunctions concentrated near the ionic cores.

A technique was developed for injecting electrons from a substrate, through a thin insulating film, and into vacuum. Scattering properties of the film were deduced from the distribution of emitted electrons. In LiF, electrons of 5 - 10 eV were found to have an attenuation length of $65 \text{ \AA} \pm 10 \text{ \AA}$. Hot electrons in CsI have an attenuation length considerably longer than 80 \AA .