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[17] An additional broad maximum has been found between the first two resonances in the corresponding reflection spectrum. This effect is not yet understood, but could be due to a possible hexagonal phase of Ne instead of the commonly adopted fcc structure.

Giant Temperature Dependence of Photoemission from the Silver Halides[*]

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Anamalous temperature-dependent photoemission has been measured from the silver halides. Structure in the photoelectron energy distributions sharpens dramatically as samples are cooled from 295 to 80°K. We believe this is due to a lattice vibrationally dependent hybridization of the halogen p and silver d valence states. Using this effect, we have experimentally located the Ag states with almost pure $4d$ symmetry at 3.7 and 3.3 eV below the highest valence states in AgBr and AgCl, respectively.

We have observed (see Figs. 1 and 2) unusually large and dramatic changes in the energy distribution curves (EDC's) of electrons photoemitted from the silver halides, upon cooling from 295 to 80°K.[1] The optical properties also exhibit striking, but less well-defined, changes upon temperature variation[2,3]; however, these effects have not been explained previously.

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 Å thick to eliminate charging at low temperatures. At room temperature, the photoemissive properties of these thin films were essentially identical to those of films 0.6 μm thick. Electron microscopy[4] and optical[3,5] 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 method[6] 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 ± 4°K. The experimental results were reproducible following temperature cycling and among different samples.

The most striking feature of the EDC's 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 0.6 to 0.3 eV upon cooling from 287 to 80°K. In both materials, room-temperature shoulders are resolved into well-defined peaks at 80°K. The higher photon energy AgBr EDC's, shown in Fig. 2, exhibit a strong new peak 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 much larger

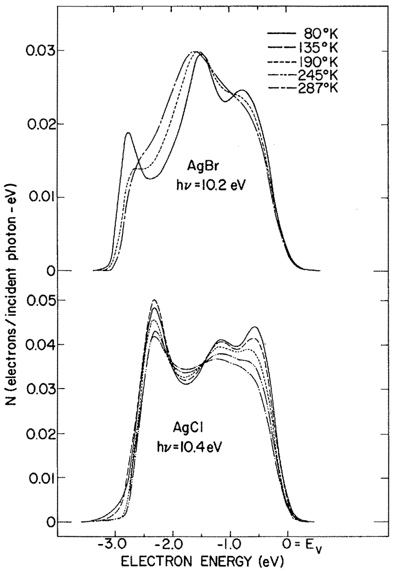

FIG. 1. Comparison of energy distributions, N, normalized to quantum yield (per incident photon) for electrons photoemitted from AgBr ($\Theta_D \approx 144$°K) and AgCl ($\Theta_D \approx 162$°K) at 80 through 287°K for photon energies of 10.2 and 10.4 eV, respectively. (The electron energy is referred 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 to absorbed photon flux because of the lack of low-temperature optical data in this photon energy range.

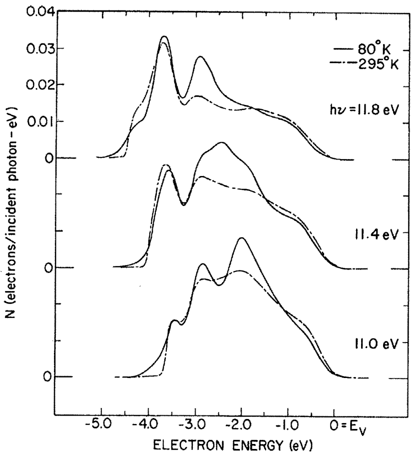

FIG. 2. Comparison of energy distributions, N, normalized to quantum yield (per incident photon) for electrons photoemitted from AgBr at 80 and 295°K for photon energies of 11.0 through 11.8 eV. (The electron energy is referred to the valence-band maximum, E_v.)

than those seen in EDC's from most materials which have been studied to date. For example, such diverse materials as Ge,[7] V_2O_4,[8] and LiI[9] show very little change in the EDC's in going from room to liquid-N_2 temperature. To illustrate this, EDC's for LiI[9] are presented in Fig. 3. In this wide variety of other solids, the changes in the photoemission EDC's upon temperature reduction are very small (comparable with the change in kT) and can be explained simply by absorption or emission of a small number of phonons. The energies involved in such a mechanism are usually too small to cause the giant variations we observe in the silver halides. 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.

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.[10] Since this wave-function overlap is dependent on the separation 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 amplitude of vibration 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 conclude that it is the thermal

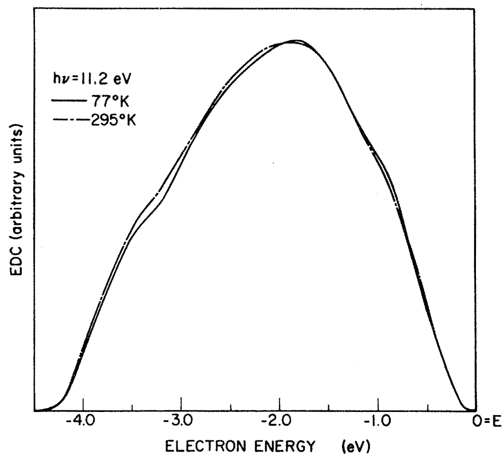

FIG. 3. Comparison of un-normalized EDC's for electrons photoemitted from LiI at 77 and 295°K for a photon energy of 11.2 eV. (The electron energy is referred to the valence-band maximum, E_v.) The heights of the curves are not significant since the scale factors were chosen arbitrarily to facilitate comparison. The data are from DiStefano (Ref. 9).

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 zero-order estimate of the magnitude of the dymanic hybridization effect, we made a tight-binding calculation[10-12] of the AgCl valence-band maximum L_3' as a function of lattice constant. Though not directly comparable with any measured EDC structure, the energy of this state provides an order-of-magnitude estimate for the experimental broadenings since its large hybridization[13] 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.[14] We have calculated the rms displacement of the ions as a function of temperature using the Debye-Waller theory.[15] Assuming an equal displacement for the two types of ions and one atom per unit cell with a mass which is the mean[16] 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.[17] 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,[10,18] 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 are of the same magnitude as the observed broadening of the photoemission EDC's (e.g., 0.6 eV for AgBr at 287°K seen in Fig. 1).

Upon cooling to 80°K, the rms ionic displacement is reduced to 0.14 Å, 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 with the 0.3-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 0.033 Å[19] since the contraction produces an L_3' shift of less than 0.1 eV upon cooling from 295 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 with 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[20,21] (i.e., for $T >$ approximately $0.1\Theta_D$). In addition, the large pressure dependence of the silver-halide absorption edge[22] 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 edge[22] gives a measure of energy level versus equilibrium ionic separation. Using this, a reduction in broadening of over 0.3 eV is found for both halides upon cooling to 80°K. This is in agreement with the estimates made above and with experiment.

It is important to note that this model predicts that the amount of change of the photoemission EDC's 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 EDC's presented in Fig. 2 for AgBr, it is seen that only certain transitions sharpen drastically upon cooling the sample. The structure on the left-hand side of this figure shows no significant changes upon temperature variation. Calculations show that the uppermost Ag 4*d* states produce very flat bands[10,18]; 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 with that found in most materials.[7-9] We thus associate the −3.7-eV peak in AgBr[1] (and similarly the −3.3-eV structure in AgCl[23]) 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 −3.7-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.[24] 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.[10]

Further credence for the dynamic hybridization is given by a Green's function approach to this problem by Doniach.[25] 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. In any case it should be exphasized that, while our zero-order calculations give credence to the proposed explanation of the temperature dependence of the optical transitions, many detailed questions remain to be answered.

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