mum varies linearly with the cube of the Ag ion separation. The independence of the energy of the Γ_1 state with respect to the halide ion indicates that the conduction states are centered on the Ag ions, in agreement with the calculations of Scop,[12] who found that the conduction band was formed principally from Ag^+ 5*s* states.

The correlation shown in Fig. 16 may be used to predict the energy of the Γ_1 state for other silver halide crystals which have the NaCl structure. If the absorption edge of the crystal is known, then the photoelectric threshold may be predicted also. By using a lattice constant of 4.92 Å, the conduction-band minimum of AgF is estimated to be at −2.5 eV. This value must be viewed in the light of the anomalous behavior often observed for fluorides. Since AgCl and AgBr form solid solutions in all proportions, the conduction-band minimum and the photoelectric threshold of mixed crystals may be estimated by using the published data for the lattice parameter[29] and for the absorption edge.[8,30] For a mixed crystal with 42% AgBr the absorption edge and lattice constant at room temperature are 2.64 eV and 5.68 Å. From Fig. 16 the energy of the Γ_1 state and the photoelectric threshold are estimated to be −3.45 and 6.1 eV, respectively. Similar estimates may be made for iodobromide and iodochloride mixed crystals and for the high-pressure phase of AgI ,which has the NaCl structure.[31–33] It would be of interest to see if the photoelectric threshold of the mixed crystals containing AgI is correlated by Fig. 16, since the absorption edge of these crystals is highly sensitive to small amounts of iodide ion.[8]

For both AgCl and AgBr Balchan and Drickamer[16] observed a blue shift of the absorption edge at temperatures above 250°C. Their observation may be explained in terms of the band-structure changes in the intermediate region (region 3, Fig. 1). For all temperatures, their shifts were calculated from the same ν_0 value—25 200 cm^{-1} for AgCl and 22 000 cm^{-1} for AgBr. At higher temperatures, it is known [1,30] that the edge shifts to the red; at 250°C, a shift of 0.2 eV (1600 cm^{-1}) was observed. Thus, the data obtained at high temperature did not correspond to the observed room-temperature transitions but to transitions involving valence states possibly 0.2 eV farther away from the valence-band maximum at L_3'. Since the *p-d* coupling term and pressure-induced energy increase of the valence state with respect to Γ_{15} decrease for values of k away from L_3', a pressure-induced blue shift at high temperatures is possible (i.e., the shift to higher energies of the valence band is less than the shift of the conduction band).

No explanation was found for the discrepancy between the present work and that of Slykhouse and Drickamer[15] concerning the AgBr absorption edge (see Fig. 13). One pertinent observation is that at the ν_0 value used by them, AgBr has a large absorption coefficient (150 cm^{-1}) which, at room temperature and atmospheric pressure, corresponds to the shoulder region of the AgBr spectrum [region 3, Fig. 1(b)]. It was in this shoulder region that the isostatic point was found both for AgBr and for AgCl.

The phonon spectrum in the silver halides should be affected by an increase in pressure, with a resulting effect on the indirect transitions in the absorption edge. However, at room temperature these effects should be overshadowed by the changes in the band structure.

At present no adequate explanation for the effect of the substrate upon the exciton peak location in AgCl is available. The peak locations for the Aclar and NaCl substrates differed by 360 cm^{-1}; however, no measurable difference was observed for the AgBr layers. It is difficult to attribute the difference to impurities, since the absorption coefficient of the AgCl is so large in this spectral region ($>10^5$ cm^{-1}).

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