FIG. 14. Phase equilibrium diagram for CuBr.

FIG. 15. Shift of CuI absorption edge with pressure.

sure, clearly involves two separate steps, spaced about 5 kilobars apart, with the absorption edge returning only part of the way at each step. Completion of the transitions with increasing pressure results in a total change in the location of the absorption edge of -2600 wave numbers. The absorption edge in the new form appears to shift blue with pressure. Between 80 and 95 kilobars, what appear to be two separate transitions take place, moving the absorption edge about 1700 wave numbers blue. In the highest pressure form, the absorption edge shifts red, with a slope of about 10.0019 ev/kilobar.

The phase equilibrium diagram obtained for CuBr is shown in Fig. 14. Because of the many phase transitions, the high-temperature runs were more difficult to analyse, although the large difference in the absorption edges, between the phase stable from 55 to 80 kilobars at room temperature, and the lowest and highest pressure forms, was helpful in determining the occurrence of transitions. The curves drawn in Fig. 13 are probably accurate within 10–15%.

Purified Reagent Grade CuI was obtained from Fisher Scientific Company, and room temperature pressure runs made up to 150 kilobars, with the same equipment used for CuCl and CuBr. The shift of the absorption edge with pressure was measured from an initial value of 23 550 wave numbers at an absorption coefficient of 15 cm^{-1}, and is shown in Fig. 15. Three distinct phase transitions took place, as indicated both by discontinuities in the shift of the edge, and by measurement of light intensity changes with pressure. These transitions occurred at 14, 41, and 80 kilobars, with changes in the location of the edge of 1300, 150, and 0 wave numbers, respectively. The slopes of the shift in the four separate phases were -0.0041, -0.0079, -0.0061, and -0.0022 ev/kilobar, in order of increasing pressure.

The direction and slope of the absorption edge shifts in the zincblende form of CuCl and CuBr are somewhat different and the shift of CuI quite different, than those of the corresponding group II–VI compounds, ZnS and ZnSe, which had blue shifts up to very high pressures,
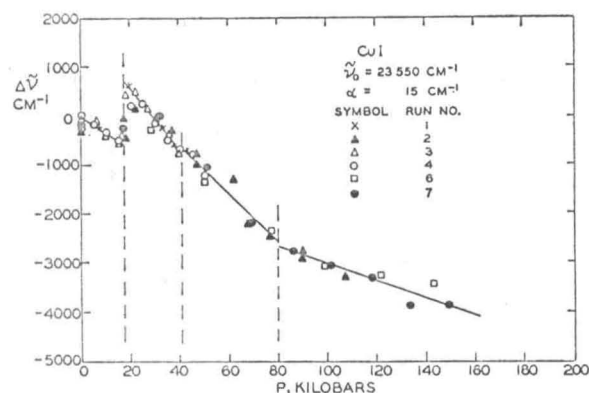
with slopes of 0.0057 and 0.0060 ev/kilobar, respectively.[2] However, the shifts of the edges are similar to those observed in the high-pressure forms of CdS and CdSe, which may have the zincblende structure. This would indicate that the band structure picture used in interpreting the results for the group IV elements Si and Ge and the group III–V compounds GaP and GaAs, and AlSb, GaSb, InP, and InAs cannot be carried over without modification, to the heavier and more ionic group II–VI compounds or any of the group I–VII compounds, which are quite ionic. Herman[24] has indicated that this is the case, because of the way the size of the energy gap changes in isoelectronic sequences. CuCl, CuBr, and CuI have smaller energy gaps than would be obtained from a reasonable extrapolation from the other members in the isoelectronic sequences, as do the high-pressure forms of CdS and CdSe, which may have the zincblende structure.

Fesefeldt and Gyulai[25] observed absorption peaks on the edges of CuCl, CuBr, and AgI, at 26 870, and 25 320, and 23 600 cm^{-1}, respectively. The peak in CuCl is largest. Gross and Kaplyanskii[26] observed this peak in a mixture of 10% CuCl in NaCl at 77°K, and found it to consist of a narrow component at 26 000 cm^{-1} and a broad component from 26 450 to 26 970 cm^{-1}. The room temperature locations found here were 26 260 and 26 600 cm^{-1} for the two components of the peak, indicating little or no temperature dependence of the peak energies.

Seitz[27] states that the peaks in CuCl and CuBr are probably due to d^{10} to d^9s transitions in the Cu^+ ion, which are allowed due to the tetrahedral symmetry of the lattice.

There is undoubtedly a crystal field splitting of these levels due to the lattice symmetry, and the effect of pressure may be further complex splitting and shifting, resulting in the observed blue shift. The loss in strength

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[27] F. Seitz, Revs. Modern Phys. 23, 328 (1951).