

with the presence of a bound vacancy, adjoining the divalent impurity (it has been shown that such vacancies are usually completely bound to the impurity atoms⁽¹⁴⁾).

It can be seen that the initial frequency shift versus pressure for these crystals follows quite a different pattern from the thallium data discussed above. In the first place, the shift is strongly dependent upon the nature of the nearest neighbor

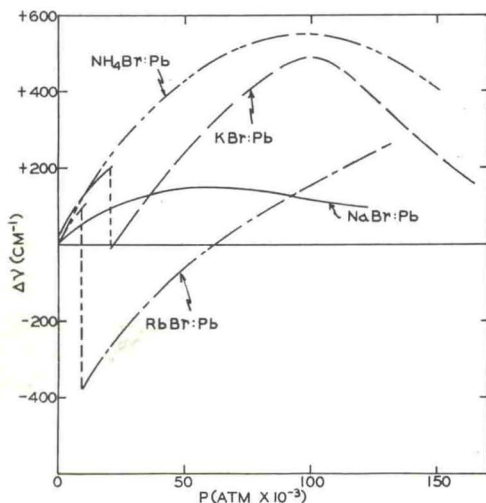


FIG. 7. "A" peak frequency vs. pressure—four alkali bromides activated by Pb^{++} .

halide ions; a dependence, moreover, which is consistent throughout the four cation systems studied. On the other hand, there is no significant difference between those crystals in the cesium chloride structure (the cesium halides) and those in the sodium chloride structure (the others). This is consistent with the complex ion model, but inconsistent with the Seitz model. This is also in agreement with the findings of FREDERICKS and SCOTT⁽¹⁵⁾ that the mobile lead-containing center in transference measurements on these crystals is negatively charged, and must therefore be a complex containing halide ions.

It should be noted here that a shift to lower energy occurs for all alkali halide phosphors, regardless of impurity or of crystal structure, given sufficiently high pressure. At these very high pressures, the system is compressed to the point where the repulsive energy is probably the dominant contribution to the crystal energy in the ground

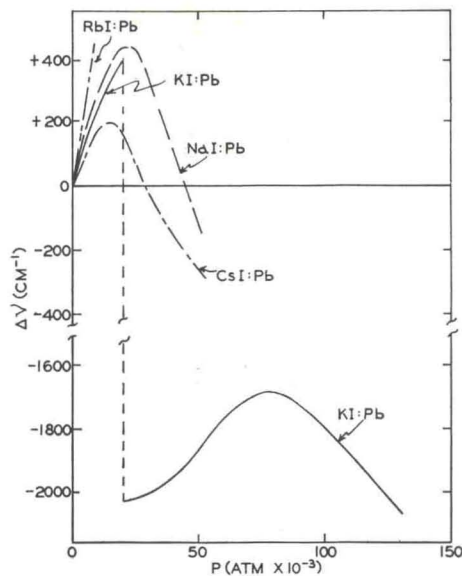


FIG. 8. "A" peak frequency vs. pressure—four alkali iodides activated by Pb^{++} .

state. This repulsive energy is very sensitive to changes in the lattice constant. The excited state probably has a flatter curve of energy vs. lattice constant than the ground state. Thus the energy

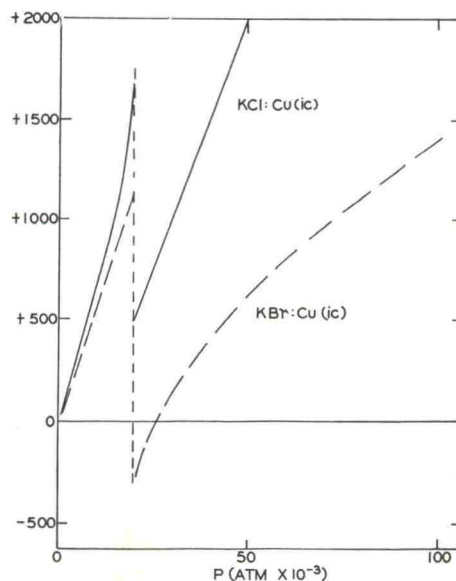


FIG. 9. "2500 Å" peak frequency vs. pressure KCl:Cu(ic) and KBr:Cu(ic).

of the ground state would increase with pressure more rapidly than the excited state energy, causing a lowering of the transition energy.

The effect of pressure on the copper ion in alkali halide lattices

Experiments with both cuprous and cupric ion impurity in alkali halides confirm the findings of BOESMAN and DEKEYSER⁽¹⁶⁾ to the effect that the absorption band at approximately 2500 Å is caused by copper in the cupric state. This band has been studied as a function of pressure to 117,000 atm in potassium bromide and to 50,000 atm in potassium chloride (see Fig. 9). Very similar shifts occur in the two cases; strongly to higher energy except at phase transitions. This leads to the conclusion that the band results from an almost completely internal transition, probably between *d* electron levels split by the crystal field.

Acknowledgements—The authors wish to thank F. E. WILLIAMS, of General Electric Research Laboratories, and A. B. SCOTT of Oregon State College for supplying us with single crystal phosphors.

R. A. EPPLER would like to acknowledge support from

a Shell Oil Company Fellowship and a Dow Chemical Company Fellowship.

REFERENCES

1. SEITZ F., *J. Chem. Phys.* **6**, 150 (1938).
2. FROMHERZ H. and MENSCHICK W., *Z. Phys. Chem.* **B3**, 1 (1929).
3. FROMHERZ H., *Z. Phys.* **68**, 233 (1931).
4. KATO M., *Sci. Pap. Inst. Phys. and Chem. Res., Tokyo* **41**, 113 (1943); **42**, 35 and 95 (1944).
5. PRINGSHEIM P., *Rev. Mod. Phys.* **14**, 132 (1942).
6. KYROPOULOS S., *Z. anorg. Chem.* **154**, 308 (1926).
7. FITCH R. A., SLYKHOUSE T. E. and DRICKAMER H. G., *J. Opt. Soc. Amer.* **47**, 1015 (1957).
8. FORRO M., *Z. Phys.* **58**, 613 (1930).
9. WILLIAMS F. E., SEGALL B. and JOHNSON P. D., *Phys. Rev.* **108**, 46 (1957).
10. LUSHCHIK N. E. and LUSHCHIK C. B., *Trud. Inst. Fiz. i Astron. Akad. Nauk Est. S.S.R.* **6**, 149 (1957).
11. HILSCH R., *Z. Phys.* **44**, 860 (1927).
12. SMAKULA A., *Z. Phys.* **45**, 1 (1927).
13. EPPLER R. A. and DRICKAMER H. G., *J. Phys. Chem. Solids* **6**, 180 (1958).
14. LIDIARD A. B., *Handbuch der Physik* Bd. **20**, S.246. Springer, Berlin (1957).
15. FREDERICKS W. J. and SCOTT A. B., *J. Chem. Phys.* **28**, 249 (1958).
16. BOESMAN E. and DEKEYSER W., *Physica, s'Grav.* **24**, 52 (1958).