

the extra streaks in the same positions but the intensities are different from those of Fig. 1, *a*.

A detailed study of the structural implications of the above findings and their possible interpretation is in progress, and the results will be published elsewhere.

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¹ Neuburger, M. C., *Z. Kristallogr.*, **93**, 314 (1936).

Crystal Structure and Photoconductivity of Cæsium Plumbohalides

WELLS¹ and his collaborators have shown that crystals of the general compositions CsPbX_3 with $X = \text{Cl}$, Br or I , and Cs_4PbX_6 with $X = \text{Cl}$ or Br , may be prepared from aqueous solutions. I have investigated the structures of these crystals and also prepared a few more. I have found² that CsPbCl_3 and CsPbBr_3 have the perovskite structure. At room temperature they are tetragonally or monoclinically distorted. Both of them, however, show transition to pure cubic perovskite structure, at 47° C. and 130° C. respectively and with cell dimensions $a = 5.605$ Å. for CsPbCl_3 , $a = 5.874$ Å. for CsPbBr_3 . Whereas no extra or forbidden X-ray reflexions can be observed above these transition temperatures, CsPbBr_3 below 130° C.—and presumably also CsPbCl_3 below 47° C.—exhibit a new structure corresponding to a doubling of the cell dimensions. The transitions are likely to be of second order as $\Delta V = 0$ within the limits of accuracy of my measurements.

The CsPbI_3 crystals from aqueous solution are orthorhombic with space group No. 62 $Pnma$ and $a = 4.795$ Å., $b = 10.457$ Å., $c = 17.76$ Å. The X-ray analysis yields all the atomic positions and interatomic distances: the lead atom is surrounded octahedrally by six iodine atoms at distances 3.01–3.42 Å., and nine iodine atoms form distorted ditrigonal pyramids around each cæsium atom at distances of 3.87–4.19 Å. The lead and iodine ions form chains of polynuclear complex ions parallel to the a -axis of the crystal. On heating these crystals to 305–308° C. they undergo a phase change and the colour changes from yellow to black. This black form which may also be obtained by melting cæsium iodide and plumbous iodide together in the correct stoichiometric proportion is rather unstable, and hence had to be investigated on a Geiger-Müller diffractometer. From its powder diagram it appears to have a monoclinically distorted perovskite structure ($a = b = 6.15$ Å., $c = 6.23$ Å., $\beta = 88.15^\circ$). It shows the same kind of superstructure as CsPbBr_3 .

It is interesting to note that the above-mentioned crystals with perovskite structure are intensely coloured: CsPbCl_3 is pale yellow, CsPbBr_3 is orange and CsPbI_3 black, whereas crystals of the type Cs_4PbX_6 with $X = \text{Cl}$, Br or I are colourless. From this peculiarity one might guess that the former crystals also have special electrical properties. With a very crude apparatus we have found that the coloured CsPbX_3 -crystals with perovskite structure are photoconductive, CsPbCl_3 having its maximum spectral sensitivity in the violet, CsPbBr_3 in the blue

to green region and CsPbI_3 in the red region, that is, the spectral region which is complementary to the colour of the crystals.

A detailed account of this work will be published elsewhere.

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¹ Wells, H. L., *Z. anorg. Chem.*, **3**, 195 (1893).

² Møller, C. K., *Nature*, **180**, 981 (1957).

Nuclear Magnetic Resonance in β -Brass

Bloembergen and Rowland¹ have shown that the addition of small amounts of zinc to copper reduces the intensity of resonance in the resulting alloy so that the line becomes unobservable when the zinc content reaches approximately 25 per cent. They explained this effect in terms of quadrupole broadening and pointed out that, in ordered structures with cubic symmetry, quadrupole broadening should be absent and a line would be expected. However, they found no resonance in a β -brass of about 50/50 composition (quoted by Bridgman² as 47.3 per cent zinc) and they suggested that the ordering was not complete.

Experiments in this laboratory have shown that there is a strong copper-63 resonance in a β -brass containing 48.33 per cent zinc by weight. The specimens were prepared by filing at room temperature and sieving through a 120-mesh sieve, annealing for 2 hr. at 450° C. in an argon atmosphere, and then slowly cooling to room temperature. The detecting apparatus was a conventional Pound-Knight-Watkins type of spectrometer operating at approximately 5.96 Mc./s. and a 'Varian' 12-in. electromagnet set at approximately 5,250 oersted. All experiments were done at room temperature.

The main features of the resonance line for the annealed powder are as follows: (1) The line is symmetrical with the centre located 5.2 kc./s. below that for well-annealed copper of 99.98 per cent purity under the same conditions. This means that the Knight shift ($\Delta H/H$) for copper in a well-ordered β -brass structure is approximately 0.14 per cent, as compared with 0.23 per cent for pure copper. (2) The integrated area under the absorption line is one-sixth of the area under a line obtained from a specimen of pure copper containing the same number of copper nuclei. (3) The line for β -brass is appreciably narrower than that for pure copper, this smaller dipole broadening being consistent with the fact that the next nearest copper neighbours are farther away than they are in pure copper. (4) The line can be eliminated almost completely by plastic deformation. This was shown by testing a specimen immediately after filing and sieving.

The detailed effects of deformation, heat treatment, and variation of composition have been studied and will be described elsewhere.

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¹ Bloembergen, N., and Rowland, T. J., *Acta Met.*, **1**, 731 (1953).

² Bridgman, P. W., *Proc. Amer. Acad.*, **84**, 131 (1955).