

07.X-9 OPTICAL ACTIVITY AND PHASE TRANSITION.  
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Optical activity of a crystal takes place when vector potential of the light beam changes over a unit cell of the crystal. In this sense, optical activity is microscopic in its nature, but must be as small as in the order of  $a/\lambda$ ;  $a$  being an atomic separation, and  $\lambda$  the wavelength. The measurements of optical activity of crystals were almost impossible without introducing serious approximations or only confined to the direction of an optic axis. Recently we developed a new method called 'HAUP' (J. Kobayashi, J. Appl. Cryst., 1983, 16, 204-211), by which optical activity of crystals of any symmetries can be measured accurately. Thus a new research field of crystal optics has now been opened. We applied it to the following problems of the phase transitions (p.t.): (1) incommensurate (i.c.) p.t., (2) electrogyration effects. As an example showing the usefulness of optical activity applications, it was found (J. Kobayashi et al. Phys. Rev., 1985, B 31, 4569-4575) that incommensurate states of the  $(\text{NH}_4)_2\text{SO}_4$  group are optically active. The origin of this effect can be understood as follows; the Fourier component of the order parameter of the i.c. phase must be complex, the free energy of the system does not then explicitly involve the phase angle of the order parameter and the transverse susceptibility becomes infinite in the i.c. phase, which means that the hamiltonian of the crystal bears continuous rotational symmetry in the two dimensional components of the order parameter and this symmetry of the hamiltonian permits the optical activity. Conversely this study directly showed that the order parameter of i.c. is complex and that two modes, phason and amplitudon must exist in this phase. We also revealed that the nearly commensurate domains which appear in the i.c. phases can be classified according to their electrogyration effects (J. Kobayashi et al. J. Appl. Cryst. 1986, 19, 377-381). In Fig. 1 one of the classes is schematically shown where the signs of the optical activity of the domains  $g_{\text{OB}}$  and soliton part  $g_{\text{S}}$  differ. This class is indeed realized in  $\{\text{N}(\text{CH}_3)_4\}_2\text{ZnCl}_4$  as seen in Fig. 2. We suggest, in summarizing these results, that the usefulness of optical activity may not be confined to the study of structurally i.c. p.t., but can be extended to reaserach on other kinds of p.t., where complex order parameters are condensed. For example, the application to magnetic, semi-conducting and superconducting transitions will be specifically promising.

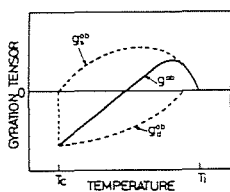


Fig. 1

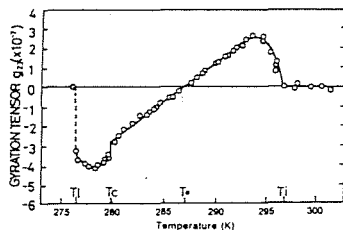


Fig. 2

07.X-10 CRYSTALLOGRAPHY OF THE HIGH CRITICAL TEMPERATURE OXIDE SUPERCONDUCTORS. By S.J. La Placa, IBM T.J. Watson Research Center, Yorktown Heights, NY 10598, U.S.A.

The discovery by Bednorz and Muller of a 40K class of high  $T_c$  oxide superconductors, and the more recent success of Chu and co-workers in reaching the 90K range, have led to a progression of scientific activity unparalleled in the history of research. After a discussion of superconductivity and its technological implications, a crystallographic and chemical overview will be given. The importance of oxygen stoichiometry and disorder will be detailed for the high temperature transformation of the 90K  $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$  phase.

07.X-11 COMPOSITION, STRUCTURE AND STABILITY OF  $\text{YBa}_2\text{Cu}_3\text{O}_x$ . By B.G. Hyde, Research School of Chemistry, Australian National University, Canberra, A.C.T., Australia [representing a group including members of the Australian National University, Canberra, A.C.T.; the Australian Institute of Nuclear Science and Engineering, Lucas Heights, N.S.W.; the C.S.I.R.O. Division of Applied Physics, West Lindfield, N.S.W.; and the University of Western Australia, Nedlands, W.A.].

Fairly pure (>95%) superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_x$  ( $x = 6.5$ ?) corrodes readily in air under ambient conditions. More extreme conditions (air saturated with water vapour at  $40^\circ\text{C}$ ) cause very rapid degradation (~25% in 16 hours). At the earliest stages lamellar faults appear in electron microscope images of the (previously perfect) orthorhombic, oxygen-deficient, "perovskite" superstructure. As the reaction proceeds, the identified corrosion products are  $\text{Ba}_2\text{Cu}(\text{OH})_2$ ,  $\text{BaCO}_3$ ,  $\text{CuO}$  and  $\text{Y}(\text{OH})_3$ .

The corrosion process quickly destroys the superconductivity. The "same" material with a lower oxygen content ( $x = 6.5$ ?) corrodes at a much lower rate, if at all, in air. It seems likely that this is because the superconductor ( $x > 6.5$ ) contains trivalent copper [Cu(III)], a powerful oxidising agent] whereas the reduced material ( $x = 6.5$ ) does not:  $\text{O}_{2.5}^{2-}$  being charge-compensated by  $\text{Y}^{3+}\text{Ba}_2^{2+}\text{Cu}_3^{2+}$ .

Various techniques are being used to investigate this and related questions.