The other Visual Pigments.—As has already been remarked, the heme pigment in its oxidised form would not suffice by itself fully to explain the observed characteristics of the spectrum even within the restricted range of wavelengths between 550 mμ and 600 mμ in which yellow is the dominant sensation. To obtain a complete picture of the situation, we have to consider also the wavelength range between 500 mμ and 550 mμ and the range between 600 mμ and 700 mμ. In these two ranges, the predominant colour sensations are those of green and red respectively. It may reasonably be inferred that we are also concerned with two other visual pigments whose contributions to the luminous efficiency are important respectively in these two regions.

It is well known that there are two other pigments chemically related to oxyhemoglobin which are known respectively as hemoglobin and hemiglobin. The first of these results from the action of reducing agents on oxyhemoglobin and the second by its auto-oxidation. It may therefore reasonably be assumed that the human retina contains three pigments based on heme whose spectroscopic behaviours are respectively similar to oxyhemoglobin, hemoglobin and hemiglobin.

Figure 4 exhibits the molecular extinction coefficients of these three pigments over the wavelength range between 500 mμ and 700 mμ, reproduced in part from the plate at the end of the book by Lemberg and Legge on *Hematin Compounds* (Interscience, New York and London, 1949). The proportions in which the three pigments are present in the retina would determine their contributions to the perception of luminosity and colour in the spectrum. In a general way, it can be seen that the superposed effects of the three pigments would explain the observed characteristics of the spectrum in respect of colour and luminosity over the range of wavelengths between 500 mμ and 700 mμ. Particularly noteworthy is the fact that a steep drop in the molecular extinction coefficient of hemiglobin appears at about 630 mμ (*see* Fig. 4), while there appears in Fig. 1 a sharp dip in the hue-discrimination curve at about the same wavelength. A steep drop in the molecular absorption coefficient of one of the visual pigments operating in this region would necessarily result in a marked improvement in hue discrimination at the same wavelength.

CRYSTAL SYMMETRY AND MAGNETIC PROPERTIES

S. BHAGAVANTAM

A CRYSTAL is built by an infinite periodic repetition in space of identical structural units. Conventionally, by the symmetry of a crystal is meant the symmetry of its spatial structure. The set of all spatial transformations which transform every point of such a structure into another point equivalent to it and also every direction into an equivalent one, forms a group which is called the space group of the crystal. There are 230 space groups and it is well known that these space groups constitute the basis for all the distinct patterns that can be identified in crystals. If we consider only the symmetry of directions at a point in a crystal, the set of all rotations and rotation-inversions which transform every direction of the structure into an equivalent direction form a group which is called the point group of the crystal. There are 32 distinct point groups of spatial transformations and these are called the 32 classes in crystallography.

The macroscopic properties of a crystal depend only on its symmetry of directions which is its point group symmetry. This dependence of the macroscopic properties of a crystal on its point group symmetry is given by Neumann's principle, which states that "every physical property of a crystal must possess at least the symmetry of the point group of the crystal". This principle, put forward by Neumann, is of fundamental significance and needs to be examined with great care in regard to the nature of physical properties one wants to deal with as well as the concept of symmetry one has in mind when one is referring to a crystal.

Since the discovery of X-rays and of even more powerful tools for investigating the internal structure of crystals, our knowledge of the crystal structure has deepened. We know that the theoretically expected spatial structure of a crystal agrees with the spatial disposition of time-average electron charge density in it and the positions of the nuclei as revealed by X-ray analysis. We are even able to explain how such a structure is responsible for several physical properties exhibited by the crystal. The successes achieved in this manner of describing the crystal structure and explaining the physical behaviour of the crystal have led to an inadvertent imposition of the point group symmetry of a crystal on all its physical properties.

That such an imposition is erroneous becomes evident when we consider certain magnetic properties of crystals which have been, till recently, elusive in a way. For instance, P. Curie conjectured the possibility of pyromagnetism and piezomagnetism being exhibited by circularly asymmetric crystals. Pyromagnetism is the appearance of magnetic moment on the application of temperature. Piezomagnetism is the appearance of magnetic moment on the application of stress. He made extensive investigations to demonstrate these phenomena but did not meet with success.

Voigt considered these effects as probable and determined the possible schemes of non-vanishing constants in respect of these properties in the 32 classical crystal classes—assuming erroneously again that these properties also, when manifest in a crystal, should possess the appropriate classical point group symmetry.

As recently as 1953, Zocher and Torok[1] analysed this situation, making use of Wigner's concept of time-inversion symmetry. Time-inversion is not a possible physical act, but can be implied as a concept in a study of a set of events in the opposite chronological order. Quantities like linear velocities are time-asymmetric. They concluded that under the operation of inversion, electric field is space-asymmetric and time-symmetric whereas magnetic field is space-symmetric but time-asymmetric. It follows that properties like magnetic moment and hence piezomagnetism and pyromagnetism are also time-asymmetric. Assuming that the structure of a crystal is time-symmetric, they concluded that time-asymmetric properties like pyromagnetism and piezomagnetism cannot exist in crystals at all.

On the other hand the Russian school appears to have been, for quite some time, cognizant of certain special features of symmetry in the structure of crystals which one has to take into account when magnetic properties are considered. In a crystal, the component parts are actually in continual motion. The distribution of electric current due to moving electrons is such that $\int J \, dV$ taken over the volume of a unit cell must vanish when averaged over time. But this does not preclude the currents from producing a macroscopic magnetic moment. The symmetry of the current distribution should correspond to that of the distribution and orientations of atomic magnetic moments. The ferromagnetic and antiferromagnetic crystals are now known to be characterised by an orderly distribution of such magnetic moments. If the crystal is built from atoms which have non-vanishing magnetic moments (spins), then this spin becomes an additional special feature of symmetry (besides its spatial symmetry) of the motif whose periodic repetition gives rise to the crystal structure.

In 1951, Shubnikov thought of spatial structures in which the motifs are geometrically identical, but can be conceived of as existing in two different forms on some other basis. He assumed them to be coloured black or white. If a spatial symmetry operation followed by a change of black into white and white into black is recognised as a single symmetry operation, which may be called a complementary symmetry operation, it can be shown that the number of distinguishable patterns increases from 230 to 1421 and the number of point groups from 32 to 90.

In ferromagnetic or antiferromagnetic structures, the neighbouring atomic magnetic moments are either parallel or anti-parallel. In such a structure, one can define a complementary symmetry operation as consisting of an ordinary spatial transformation followed by a reversal of spins. It may turn out that a usual symmetry operation of spatial transformation, while bringing the geometrical structure into coincidence with itself, may result in the reversal of the orientation of spins. In such a case the complement of that operation as defined above will be a symmetry operation. It may be pointed out here that a reversal of spins corresponds to a reversal of micro-currents that are responsible for the magnetic moments. This, in essence, is not different from the concept of time-inversion.

The recognition of new complementary symmetry operations increases the possible number of crystal classes to 90. We can call them magnetic point groups or magnetic classes. They include the 32 classical point groups. For a simple derivation of the magnetic classes one may refer to a recent publication by Bhagavantam and Pantulu.[2]

The ferromagnetic and antiferromagnetic

structures possess either ordinary operations or complementary operations or both as symmetry operations, but the single operation of reversal of spins is not a symmetry operation for them. Such structures may be described as being time-asymmetric. It is at once evident, as pointed out by Dzialoshinskii,[3] that arguments put forward to show that pyromagnetism and piezomagnetism are not possible are valid only for paramagnetic crystals. In fact he showed that it is possible for substances possessing antiferromagnetic structures to exhibit piezomagnetism. In 1955, Borovik-Romanov[4] confirmed these predictions by demonstrating the existence of piezomagnetic effect in CoF_2 and MnF_2 and measuring the dependence thereof on temperature in CoF_2.

We can here go back to the general problem of crystal symmetry and its influence on physical properties. It will be helpful to remind ourselves that there is no absolute definition for the symmetry of a crystal or of any object. There is always a context or attitude with reference to which the symmetry of an object is understood and described. The fact that almost all animals have a bilateral symmetry of external form, but that no such symmetry exists if the structure of their internal organs is taken into account is an easily understood example from the field of biology. Likewise the result of an experimental determination of the point group symmetry of a crystal depends on the kind of external means we choose to apply and observe its effect. For example, the study of the Laue patterns reveals only 11 distinct classes and not 32. Such methods cannot in themselves give direct information on the presence or absence of a centre of symmetry. In fact, every crystal diffracts X-rays as if a centre of symmetry were present.

The term "symmetry of the crystal" needs qualification in view of the generalisations mentioned. If it is a magnetic property which is influenced by the magnetic structure in a crystal that we wish to discuss, the appropriate magnetic class of the crystal defines the symmetry of the crystal. In a similar manner we have to amplify Neumann's principle. If the physical property under study depends on the magnetic structure of the crystal in which it is observed, Neumann's principle should be understood as laying down that the physical property possesses at least the magnetic point group symmetry of the crystal.

That these generalisations in the concept of symmetry are significant can be seen from the results given by Bhagavantam and Pantulu.[2] In that work, a group theoretical method given earlier by Bhagavantam to obtain the number of non-vanishing independent constants of a physical property subject to a point group symmetry has been extended to obtain similar results for pyromagnetism, magnetoelectric polarizability and piezomagnetism in respect of the 90 magnetic classes. It has been shown that the property of pyromagnetism is possible in 31 classes. 14 of these 31 classes are from the classical point groups and would be the only ones recognised as pyromagnetic classes, if spatial symmetry alone is taken into account. The remaining 17 classes arise out of the possibility that each classical point group can give rise to magnetic variants. A magnetic variant is a magnetic class derivable from the classical class. If the concept of magnetic symmetry is not recognised, all crystals possessing the spatial symmetry appropriate to the classes of which these seventeen are magnetic variants would have been regarded as incapable of exhibiting pyromagnetism. Similar considerations can be extended to other properties.

A particular example in piezomagnetism which received experimental confirmation may also be mentioned. CoF_2 and MnF_2 belong to the magnetic crystal class $4/m\,\underline{m}\,\underline{m}$ Piezomagnetism for this crystal class is characterised by two independent non-vanishing constants. This has been experimentally verified by Borovik-Romanov. On the other hand, if we treat the crystals as belonging to classical crystal class $4/m\,m\,m$, ignoring magnetic symmetry, piezomagnetism is still possible but should be characterised by only one independent non-vanishing constant.

From these considerations it is evident that the generalisations in regard to the concepts of symmetry discussed in the foregoing pages are of great significance while studying the physical properties of crystals.

1. Zocher, H. and Torok, C., *Proc. Nat. Acad. Sci.*, 1953, **39**, 681.
2. Bhagavantam, S., and Pantulu, P. V., *Proc. Ind. Acad. Sci.*, 1964, **59**, 1.
3. Dzialoshinskii, I. E., *Soviet Physics*, J.E.T.P., **1958**, **6**, 621.
4. Borovik-Romanov, A. S., *Ibid.*, **1959**, **9**, **1390**.