PLANE DICHROMATIC SPACE GROUPS

T. S. G. KRISHNAMURTY AND P. GOPALAKRISHNAMURTY
Andhra University, Waltair

THE ordinary crystallographic theory in two dimensions, making use of anti-symmetry operations, was first extended by Alexander and Hermann[1,2] (1928, 1929) when the possible symmetries of liquid cystals are studied. Starting from the 17 two-dimensional conventional space groups they derived 80 space groups when both sides of a plane are regarded as distinct. These 80 groups can be divided into three categories, namely, (*i*) the ordinary 17 space groups, (*ii*) the 17 grey space groups containing the anti-identity operation explicitly and (*iii*) the 46 double-coloured (dichromatic) magnetic space groups which can also be designated as the magnetic variants of the space groups. Cochran[3] in order to describe fully the symmetry properties of real periodic functions in two dimensions employed in crystallography has enumerated these 46 dichromatic space groups with the help of the six reversal symmetry operations. Further references concerning the methods of derivation of the magnetic space groups in a plane are to be found in the review article of Mackay.[4] In this note the 46 magnetic double-coloured space groups are derived from the representation theory of the conventional space groups employing the method indicated earlier by the authors (Krishnamurty and Gopalakrishnamurty).[5] Several interesting features noted in the course of the derivation of the magnetic variants of the space groups in a plane are described here in detail.

A Brief Outline of the Method

It has already been pointed out by the authors[5] that the magnetic variants of a space group can be obtained from the non-equivalent alternating representations of the symmorphic (point) space group, which is reciprocal to the underlying point space group of the given space group. For instance, the underlying point space group of *pmg* and *pgg* in two dimensions is *pmm* and its reciprocal point space group is *pmm* itself. Thus one may infer that the magnetic variants of all those conventional space groups having the same underlying space group can be derived from the alternating representations of the symmorphic space group which is reciprocal to that underlying space group. Though the alternating representations of the reciprocal symmorphic space group, no doubt, induce the magnetic variants of a space group, yet in enumerating the magnetic variants, the distinct features of the symmetry elements of the given space group have to be taken into account in deciding the equivalence among the inducing alternating representations. Since the only lattices encountered in two dimensions are either primitive (*p*) or side-centered (*c*), it is sufficient to note that if a crystal lattice is primitive or side-centered, its reciprocal lattice is primitive or side-centered.

If T_x and T_y are the basic translations along the Bravais axes in two dimensions, T_x and T_y can be represented (Koster[6]) respectively by exp. $(2\pi i k_x)$ and exp. $(2\pi i k_y)$, where k_x and k_y are the components of the wave-vector $\vec{k}$ belonging to the reciprocal space. It is enough (Krishnamurty and Gopalakrishnamurty[7]) to consider the equations $T_x{}^2 = T_y{}^2 = E$ (identity) in enumerating the magnetic variants of a space group. This restricts the choice of the admissible values of the k_x and k_y to either 0 or $\frac{1}{2}$. Hence in the construction of the dichromatic magnetic space groups in two dimensions we need consider only those stars containing any one (Krishnamurty and Gopalakrishnamurty[8]) of the wave vectors: $(0, 0)$, $(0, \frac{1}{2})$, $(\frac{1}{2}, 0)$ and $(\frac{1}{2}, \frac{1}{2})$ from the 13 distinct reciprocal point space groups in terms of whose alternating representations, the magnetic variants of the 17 conventional space groups can be derived.

Classification of Space Groups

The alternating representations of a crystallographic space group can be enumerated by considering the generating elements of the space group. The maximum number of the generating elements of a conventional space group in two dimensions will be 4 and their characters in the alternating representations will be ± 1. An alternating representation of an ordinary space group in which the characters of T_x and T_y are alone equal to $+1$ will induce a dichromatic magnetic space group hereafter designated as a point group variant of the space group. The dichromatic space groups induced by the alternating representations, which correspond to the distinct stars[5] containing a non-zero wave vector, of the reciprocal symmorphic space group, are referred to as translational group variants of the space group. Further one may easily see that if all the generating elements are represented by the character $+1$ in an irreducible representation of a space group, then the corresponding induced magnetic space group cannot be distinguished from the given conventional space group. For purposes of enumeration of the double-coloured magnetic space groups, it is found convenient to express them as the sum of the two kinds of the variants: (*i*) the point group variants and (*ii*) the translational group variants. Thus in what follows the conventional space groups in two dimensions are accordingly divided into two categories.

Derivation of the Plane Dichromatic Space Groups

For convenience and purposes of clarity the 17 two-dimensional space groups are classified hereunder into two categories, namely, I: *p*1, *p*2, *p*4, *p*3, *p*3*m*1, *p*31*m*, *p*6 and II: *pm*, *pg*, *cm*, *pmm*, *pmg*, *pgg*, *cmm*, *p*4*m*, *p*4*g* and *p*6*m*. It is well known that the point group symmetries of the 17 space groups belong to one or other of the 10 crystallographic point groups in two dimensions. The number of the double-coloured magnetic point groups corresponding to each one of the 10 ordinary point groups in a plane is given below in brackets against the appropriate point group: 1 (0); 2(1); 4(1); 3(0); 3*m* (1); 6(1); *m* (1); 2*mm* (2); 4*mm*(2) and 6*mm*(2). The magnetic variants of the 7 plane space groups of category I whose underlying point groups are 1, 2, 4, 3, 3*m* and 6 have been enumerated and expressed in Table I directly as the sum of the point group variants and the translational group variants of the space groups.

TABLE I

No.	Space group	Lattice	No. of point group variants	No. of translational group variants	No. of the induced dichromatic magnetic space groups
1	*p*1	Monoclinic	0	1	1
2	*p*2	,,	1	1	2
3	*p*4	Tetragonal	1	1	2
4	*p*3	Hexagonal	0	0	0
5	*p*3*m*1	,,	1	0	1
6	*p*31*m*	,,	1	0	1
7	*p*6	,,	1	0	1
		Total ..	5	3	8

In this way, the 8 dichromatic magnetic variants of the 7 space groups of category I are described.

The point groups of the remaining 10 two-dimensional space groups belonging to category II are *m*, 2*mm*, 4*mm* and 6*mm*. The double-coloured magnetic space groups of *pmm*, *pmg* and *pgg* classified under category II will now be considered in detail. For the above three space groups, the underlying point space group is *pmm*, whose reciprocal space group is *pmm* itself as has been mentioned earlier. It will now be shown that the double-coloured magnetic space groups associated with *pmg* and *pgg* can be obtained from the alternating representations of *pmm*. The generating elements of *pmm* may be taken as σ_x, σ_y, T_x and T_y.

The 16 one-dimensional real irreducible representations of *pmm* can be uniquely described by the relations:

$$\sigma(\sigma_x) \rightarrow \pm 1,\ \sigma'(\sigma_y) \rightarrow \pm 1,\ T(T_x) \rightarrow \pm 1 \text{ and } T'(T_y) \rightarrow \pm 1.$$

The character Table of *pmm* constructed in terms of the 4 generating elements is given in next page.

Taking isomorphism among the subgroups of index 2 associated with the 15 irreducible representations of *pmm* into account, the 15 alternating representations of *pmm* are grouped into the following classes so far as the derivation of the dichromatic magnetic space groups of *pmg* is concerned: (*i*) A_5, A_6, A_9, A_{10}; (*ii*) A_7, A_8, A_{11}, A_{12}; (*iii*) A_{13}, A_{14}, A_{15}, A_{16}; (*iv*) A_2; (*v*) A_3 and (*vi*) A_4. Here the alternating representations in a class are equivalent. It may be noted that in the case of *pmg*, σ cannot be regarded as equivalent (isomorphous) to σ' since the latter is a glide plane while the former is a mirror plane. Establishment of isomorphism among the associated subgroups of index 2 is facilitated by noting that the basic translations T and T′ of the orthorhombic primitive lattice can be interchanged which means the equivalence[8] of the stars *b* and *c* of the space group *pmm*. The non-equivalent alternating representations of *pmm* corresponding to the classes (*i*), (*ii*) and (*iii*) induce the magnetic double-coloured space groups called the translational group variants, while those corresponding to the classes (*iv*), (*v*) and (*vi*) induce the magnetic variant space groups referred to as the point group variants. Thus the total number of the dichromatic magnetic space groups associated with *pmg* is 6. The

Character table of pmm

Star	Irreducible representations	σ	σ'	T	T′	Associated* subgroups of index 2	Rational symbol (Shubnikov and Belov[9]) of the induced dichromatic space groups
a (0, 0)	A_1	1	1	1	1	..	..
	A_2	1	−1	1	1	H_2 (σ, T, T')	*pmg′*
	A_3	−1	1	1	1	H_3 (σ', T, T')	*pm′g*
	A_4	−1	−1	1	1	H_4 $(\sigma\sigma', T, T')$	*pm′g′*
b (0, ½)	A_5	1	1	1	−1	H_5 $(\sigma\sigma', T', T)$	..
	A_6	1	−1	1	−1	H_6 $(\sigma, \sigma'T', T)$	$p_b'mg'$
	A_7	−1	1	1	−1	H_7 $(\sigma', T, \sigma T')$	$p_b'gm$
	A_8	−1	−1	1	−1	H_8 $(\sigma T', \sigma'T', T)$	..
c (½, 0)	A_9	1	1	−1	1	H_9 (σ, σ', τ')	..
	A_{10}	1	−1	−1	1	H_{10} $(\sigma, \sigma'T, T')$	..
	A_{11}	−1	+1	−1	1	H_{11} $(\sigma', T', \sigma T)$	..
	A_{12}	−1	−1	−1	1	H_{12} $(\sigma T, \sigma'T, T')$	..
d (½, ½)	A_{13}	1	1	−1	−1	H_{13} (σ, σ', TT')	$p_c'mg$
	A_{14}	1	−1	−1	−1	H_{14} $(\sigma, \sigma'T, TT')$	..
	A_{15}	−1	1	−1	−1	H_{15} $(\sigma', \sigma T', TT')$	..
	A_{16}	−1	−1	−1	−1	H_{16} $(\sigma'T, \sigma T', TT')$	..

* The symmetry elements given in brackets against a subgroup of index 2 in this table are the generating elements of the subgroup.

double-coloured magnetic space groups of *pmm* can be deduced from those of *pmg* by ignoring the fractional translation present in σ' of *pmg* and hence treating σ and σ' to be equivalent. From this, the classes (*i*) and (*ii*), (*iv*) and (*v*) can be clubbed together to give rise to only four distinct classes. Consequently, four dichromatic magnetic space groups correspond to *pmm*.

The magnetic variants of the space group *pgg* stand on equal footing with those of *pmm* since fractional translations are involved in both the reflection planes of *pgg*. The remaining space groups of category II can be treated on similar lines and the results so obtained concerning the 10 space groups of the second category are summarised in Table II.

The 46 magnetic variants of the two-dimensional space groups so enumerated are given in Tables I and II.

TABLE II

No.	Space group	Lattice	No. of point group variants	No. of translational group variants	Total no. of the induced dichromatic space groups
1	*pm*	Orthorhombic	2	2	4
2	*pg*	,,	2	2	4
3	*cm*	,, side-centered	1	1	2
4	*pmm*	Orthorhombic	2	2	4
5	*pmg*	,,	3	3	6
6	*pgg*	,,	2	2	4
7	*cmm*	,, side-centered	2	1	3
8	*p4m*	Tetragonal	3	1	4
9	*p4g*	,,	3	1	4
10	*p6m*	Hexagonal	3	0	3
		Total ..	23	15	38

DISCUSSION

It may be interesting to note that in the case of the two-dimensional space groups *p4m* and *p6m* the number of the double-coloured magnetic space groups (Table II) described here as the point group variants is 3, whereas the number of the magnetic variants of the respective underlying point groups 4*mm* and 6*mm* is 2 only. This is because the equivalence between 2 σ_v and 2 σ_v' of 4*mm*, 3 σ_v and 3 σ_v' of 6*mm* (Bhagavantam and Venkatarayudu[10]) present in the point groups is destroyed by the translations of the space group. The translations in a space group will be responsible for the non-equivalence of two conventional symmetry operations which are otherwise regarded as isomorphous (equivalent) in the underlying point group. One may also add that the double-coloured magnetic variants of a crystallographic space group referred to here as the point group variants are induced by the alternating representations of the factor group of the reciprocal point space group.

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1. Alexander, E. and Hermann, K., *Z. Kristall.*, 1928, **69**, 285.
2. — and —, *Ibid.*, 1929, **70**, 328.
3. Cochran, W., *Acta Cryst.*, 1952, **5**, 630.
4. Mackay, A. L., *Ibid.*, 1957, **10**, 543.
5. Krishnamurty, T. S. G. and Gopalakrishnamurty, P., "Dichromatic Shubnikov space groups," *Curr. Sci.*, 1968, **37**, 638.
6. Koster, G. F., *Solid State Physics*, 1957, **5**, 173.
7. Krishnamurty, T. S. G. and Gopalakrishnamurty, P., A paper on "Magnetic Symmetry Groups," Communicated to *Acta Cryst.*, 1968.
8. — and —, "A note on the derivation of magnetic lattices" *Curr. Sci.*, 1968, **37**, 574.
9. Shubnikov, A. V. and Belov, N. V., *Coloured Symmetry*, Pergamon Press, Oxford, 1964, p. 214.
10. Bhagavantam S. and Venkatarayudu, T., *Theory of Groups and its Applications to Physical Problems*, Andhra University, 1951, p 124.

A METHOD FOR THE ESTIMATION OF TOTAL SOLUBLE COBALT IN SEA-WATER*

T. M. KRISHNAMOORTHY, V. N. SASTRY AND T. P. SARMA

Bhabha Atomic Research Centre, Health Physics Division, Bombay-74 (AS)

THE estimation of cobalt in sea-water has been done by various workers[1-4] using colorimetry and activation analysis methods. In view of the extremely low content of cobalt in sea-water (0·1–1·0 μg./1), co-precipitation methods have been used for preliminary concentration of the element. Yamagata and Iwashima[5] added powdered manganese dioxide to sea-water which scavenges cobalt along with other trace elements. The recoveries are established to be 100% using cobalt-60 in the chloride form as tracer. Krishnamoorthy and Viswanathan[4] have co-precipitated cobalt along with magnesium hydroxide by adding KOH solution to sea-water and the recoveries are established to be 93% using cobalt-58 in the chloride form as tracer.

Cobalt is one of the biologically active elements which is taken up by the phytoplankton and algæ from sea-water. Preliminary laboratory studies[6] indicated that cobalt can be associated in significant amounts with soluble organic matter. From the work reported in the literature, it is not established whether cobalt associated with soluble organic matter is also carried in the initial concentration steps used. Experiments have been carried out to find whether any differences exist in the recovery of cobalt if it is present in the ionic form as well as in the organic form.

Three litres of sea-water filtered through Whatman No. 42 filter-paper is spiked with $Co^{58}Cl_2$ tracer and magnesium is precipitated as hydroxide using 10 ml. of 4 N NaOH. Cobalt-58 gamma activity in the precipitate is counted and compared with the standard added. The recoveries are found to be 96–98% and these results are given in Table I.

TABLE I

Co-precipitation of cobalt-58 with magnesium hydroxide

No.	Co-58 activity in solution after 40 hrs. equilibration cpm	Co-58 activity in $Mg(OH)_2$ ppt. cpm	Activity in supernatant liquid (before filtration) cpm	Activity in supernatant liquid (after filtration) cpm
1	106,652	102,500 (96%)	1875 (1·8%)	1200 (1·2%)
2	108,000	105,600 (98%)	656 (0·7%)	488 (0·5%)

Activity of cobalt-58 added to the solution 106,700 cpm.

Chlorella sp. is grown in sea-water spiked with $Co^{60}Cl_2$ tracer to get organically bound cobalt.[6] The supernatant of the culture solution is filtered through 0·22 μ millipore membrane filter. An aliquot of the culture solution containing soluble cobalt (organically bound and/or otherwise) is added to 3 litres of filtered sea-water and magnesium is precipitated as hydroxide as above. The precipitate is allowed to settle for 2 hours and the supernatant liquid decanted. The slurry

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