牛津大学研究生教材

固体对称性数学理论

点群和空间群的表示理论

C.J.布拉德利，A.P.克拉科尼尔

世界图书出版公司
www.wpcbj.com.cn

固体对称性的数学理论

点群和空间群的表示理论

C. J. 布拉德利
A. P. 克拉科尼尔 著

图书在版编目（CIP）数据

固体对称性数学理论 = The Mathematical Theory of Symmetry in Solids：英文/（英）布拉德利（Bradley，C. J.）著．—影印本．—北京：世界图书出版公司北京公司，2012. 9
ISBN 978 - 7 - 5100 - 5279 - 8

Ⅰ．①固…　Ⅱ．①布…　Ⅲ．①固体物理学—教材—英文　Ⅳ．①O48

中国版本图书馆 CIP 数据核字（2012）第 217121 号

书　　名：	The Mathematical Theory of Symmetry in Solids: Representation Theory for Point Groups and Space Groups
作　　者：	C. J. Bradley, A. P. Cracknell
中 译 名：	固体对称性数学理论
责任编辑：	高蓉　刘慧
出 版 者：	世界图书出版公司北京公司
印 刷 者：	三河市国英印务有限公司
发　　行：	世界图书出版公司北京公司（北京朝内大街 137 号 100010）
联系电话：	010 - 64021602，010 - 64015659
电子信箱：	kjb@ wpcbj. com. cn
开　　本：	16 开
印　　张：	47. 5
版　　次：	2013 年 1 月
版权登记：	图字：01 - 2012 - 6226
书　　号：	978 - 7 - 5100 - 5279 - 8　　定　价：155. 00 元

影印版前言

自从上世纪80年代起，世界图书出版公司北京公司一直致力于与世界各国知名出版商合作，是国内最早开展购权影印图书出版工作的机构。时至今日，已经持续近30年，不仅引进的品种数独占鳌头，而且包括了大量在国际上具有深远影响的经典图书，受到了国内学者和专家的认可和好评。

现在应国内广大读者的要求，在获得牛津大学出社授权的前提下，世界图书出版公司北京公司将陆续影印出版该社各类丛书中的经典图书。牛津大学出版社是世界著名出版机构之一，每年出版的书籍、刊物超过四千种，其学术著作和教科书的作者均为相关领域的著名学者，其中不乏科学研究前沿的顶尖科学家和领军人物，书籍内容涵盖了最新的科学进展的各个方面，因此一直受到国内外科研人员和高校师生的高度评价，其中已经出版的数学和物理学系列丛书，如*Oxford Graduate Texts in Mathematics*，*Oxford Graduate Texts*，*Oxford Lecture Series in Mathematics and Its Applications*和*Oxford Mathematical Monographs*在国内有着广泛的影响，受到普遍好评。

毫无疑问，考虑到我国的国情以及科学教育发展的迫切需要，这项工作的最大受益者将是那些经济尚不富裕，但却渴望学习知识，想及时了解最新科学技术成果的国内高校和研究机构中的莘莘学子，相对原版，影印版的价格他们更容易接受。在这里，中国的读者和我们出版公司要特别感谢牛津大学出版社以传播科技知识为重，授权世界图书出版公司北京公司影印出版该社系列丛书中的部分图书。我们相信，这些图书的引进，不仅会受到数学物理等相关专业的教师和研究生的欢迎，相关领域的科研人员也将会从中受益。

前　　言

正如副标题所指出的，本书介绍了点群和空间群不可约表示的推导及其数学用表，同时包括确定属于这些表示的对称适化函数的讨论。本书还讨论了磁点群和空间群的余表示。当然，大部分确定空间群表示的理论都已经可以在文献中得到，但是它们非常零散，并且，不同作者采用不同的标记方法。空间群表示的两组用表已经发表了一段时间了（Faddeyev，1964和Kovalev，1965），但是它们都没有包含这些表示对应的理论或者性质的综合阐述。在本书手稿的最后准备阶段，Miller和Love（1967）的研究成果发表了；而在本书的校对阶段，Zak，Casher，Glück和Gur（1969）的成果也发表了。利用这些成果，我们核对了书中给出的许多用表。

本书给出了230个空间群在Brillouin区中的每个对称点处和沿着每一条对称线的波矢k的群之单值和双值表示的完整用表。这些用表包括所有相关的抽象有限群（秩≤192），而且利用适当的抽象群，我们确定了每个波矢k的群。在这些用表中，我们既给出了特征标表也给出了矩阵表示。有几个表是通过计算机推导或者检验的，例如表2.6，5.1，5.7和6.8，但我们没有给出其中涉及的计算技巧的描述，建议读者参考，例如，由Canon（1969）所写的关于计算机和群论的综述文章。表6.13和表5.7 的一致性还用手工检验了，请看第468页的脚注。个别的一些空间群用表也已经和Faddeyev，Kovalev，Miller和Love，Zak，Casher，Glück和Gur等人给出的表比对过了。但是，要和所有已知的用表去完全、详尽地比对是不可能的，因为不同的作者采用了不同的标记方法和约定。如果本书这些表的一切项目都是正确的，那的确将是非常了不起的。如果读者能够告知可能发现的任何错误的细节，我们将非常感谢。物理研究所已经做好了安排，发表那些以信的形式寄给Journal of Physics C: Solid State Physics.的编辑，从而引起了我们注意的这类错误。

我们已经尽可能多地包括了对布拉维晶格、点群和空间群的数学晶体学看来必要的描述，但是读者可能发现，参考一本晶体学教材或者《国际X射线晶体学用表》（Henry和Lonsdale，1965），将会大有益处。在第3章，我们给出了空间群表示理论的部分完整的描述。而全部完整的理论在第4章给出，其中我们用了一种一般的标记法处理了该理论，这使得我们不仅涵盖了空间群理论，而且还得到了一种在固体理论之外的其他应用中都有用处的理论。所以，作为诱导与分道（subduced）表示理论的初步学习，希望第4章

的那些部分对工作于各个领域的的工作者都有帮助，而不仅仅只是对固体物理学者才有用。我们假设本书的读者具备群论和群表示理论的基本知识，然而在1.2节和1.3节我们也把该理论的相关部分作了总结。

一些内容被忽略是完全必要的。我们省略了晶体中张量的对称性性质的任何讨论，一是因为它对群表示理论用处不大，二是因为在非磁晶体（Nye，1957）和磁性晶体（Birss，1964）中的张量对称性性质的论题已经有了充分的论述。尽管我们在第7章中给出了磁空间群余表示的详细描述，并且举了一些例子，但是在可用的空间给出所有1191个黑和白磁空间群的不可约余表示的用表是不切实际的，这些表已被Miller和Love（1967）给出了。我们本来想把可以应用该理论以及我们所给出的表的那些领域给出详细的讨论的。然而，既没有空间也没有时间可以用来适当地做这件事，因为这可能需要第二部这样大的一卷书。。因此，在本书适当的地方，我们简单地指明了可能的物理应用，同时给出了一些合适的参考文献或者综述文章。最后，我们省略了非晶体学点群的任何讨论，这是因为它们并不适合出现在一部主要讨论固体而不是分子的书中。

非常感谢D. L. Altmann博士，他最早鼓励我们撰写本书并以相当大的兴趣关心书的进展情况。也要感谢那些在写书的各个阶段就本书内容或者参考文献与我们进行了许多有益的讨论和通信的各位；J. S. Rousseau博士和N. B. Backhouse博士仔细阅读了本书的每一章，从而消除了很多错误；B. L. Davies博士把第2章中立方晶格谐波用表从小数点后第8位数的精确度提高到了第11位，同时对第7章的部分内容和俄文参考文献给予了很大帮助。R. J. Elliott博士、G. Harbeke博士和K. L. Jüngst博士各自独立地检查了第2章中晶格谐波用表并相继提出了一些修正。D. Litvin博士、R. Loudon教授和W. Marzec博士提供了Kovalev（1965）表的勘误表。K. Olbrychski博士、M. Schulz博士和J. Staněk先生帮助我们完成第7章的索引，D. E. Wallis先生撰写了计算机程序来检查表5.1。我们还要感谢R. H. Whittaker先生和J. Zak教授。作者之一（A.P.C.）想指出以下事实：对本书写作的贡献大部分是在以前受雇于新加坡大学物理系和英国埃塞克斯大学时完成的，他要感谢以前的同事在这段时间对他的鼓励。感谢所有的作者、编辑和出版商，他们允许复制有版权的图和表，这些图和表的出处都在原来的位置适当地标明了。最后，感谢牛津大学出版社的员工在本书出版过程中所给予的关照。

C. J. Bradley

A. P. Cracknell

1969年8月

2009年重印版前言

我们写本书初版的时候，正在开始做一些关于金属能带结构方面的工作，我们强烈地意识到缺少一本介绍空间群和磁群的不可约表示及其余表示用表的书。在我们完成本书之前，一些作者采用了完全不同的标记，发表了相似的表，他们的名字在参考文献中列出了。本书的独特之处在于：（1）内容完整；（2）非常详细地涵盖了点群和空间群表示用表背后的理论；（3）对于每个简并表示，除了特征标表，还给出了矩阵表示集合。本书初版很早以前就已售缺，连二手的复印件都很难找到。所以，我们非常高兴、同时也感到荣幸的是牛津大学出版社重印了本书，提供更容易获取的涉及目前这一代人的内容。

本书初版中有一些错误，现在是改正它们的机会。这些错误的数量非常少，因此必须称赞初版排字员和校对者极大的耐心和对细节的关注。

C. J. Bradley

A. P. Cracknell

2009年6月

目　　录

第1章　对称性和固态

1.1　简介 1
1.2　群论 7
1.3　群的表示 15
1.4　点群 24
1.5　空间群 37

第2章　点群的对称适化函数

2.1　转动群的矩阵元 51
2.2　对称适化函数的生成 54
2.3　点群中的应用 56
2.4　晶体点群的对称适化函数 57
2.5　主动和被动算子 76
2.6　点群表示的对称化和反对称化乘积 77

第3章　空间群

3.1　布拉维格子 81
3.2　倒格子和布里渊区 86
3.3　点对称和线对称的分类 95
3.4　平移群的不可约表示 119
3.5　230个三维空间群的分类 121
3.6　对布洛赫函数的空间群的运算 144
3.7　空间群表示理论的描述说明 146
3.8　举例：立方密堆积和金刚石结构 161

第4章 根据不变子群表示的群表示

4.1 诱导表示 171
4.2 具有不变子群的群 176
4.3 小群理论 181
4.4 小群的小表示 184
4.5 作为半直积的点群 186
4.6 小群诱导表示的实现 201
4.7 诱导表示的直积 204
4.8 诱导表示的对称化和反对称化平方 215

第5章 230个空间群的单值表示

5.1 抽象群 225
5.2 230个空间群的单值表示 285
5.3 空间群表示用表 389
5.4 空间群表示用表的使用举例 397
5.5 表示域和基本域 407

第6章 32个点群和230个空间群的双值表示

6.1 点群的双值表示 418
6.2 双点群的对称适化函数 437
6.3 空间群的双值表示 454
6.4 双空间群表示的推导举例 458
6.5 230个空间群的双值表示 467

第7章 磁群及其余表示

7.1 舒勃尼科夫群及其推导 569
7.2 舒勃尼科夫群分类 570
7.3 反幺正运算和磁群的余表示 605
7.4 余表示的克罗内克积 618
7.5 磁点群的余表示 622
7.6 磁空间群的余表示 638
7.7 举例：P_2'/mnm'的空间群余表示及其克罗内克积 652

7.8 自旋空间群 669
7.9 多色点群和空间群 677

附录

参考文献

主题索引

1

Symmetry and the solid state

1.1. Introduction

THE history of man's interest in symmetry goes back many centuries (Belov 1956*b*, Coxeter and Moser 1965, Steno 1669), but its study on a modern scientific basis can be considered to have been started by the Abbé Haüy. Haüy studied the behaviour of a specimen of calcite when it was cleaved and, by breaking it into smaller and smaller pieces and studying the angles between the faces of the fragments, he convinced himself that the crystal was made up by the repetition of a large number of identical units. Haüy (1815*a*–*d*) studied many other crystals as well and summarized his conclusions in his so-called *Loi de symmétrie*. The study of symmetry developed through the nineteenth century with the formulation of ideas about point groups, Bravais lattices, and space groups.

A *point group* is a set of symmetry operations acting at a point and obeying the requirements that they should form a group in the mathematical sense; the crystallographic point groups satisfy the extra requirement that they must be compatible with a space lattice. Only a finite number of different combinations of symmetry operations are observed to occur in real crystals. The derivation of these 32 point groups was published by Hessel (1830) but his work was neglected for over 30 years until they were derived again by Gadolin (1869). Since then the point groups have been studied extensively, both in their original crystallographic context and, more recently, in the context of group-theoretical studies of the physics and chemistry of molecules and solids. There are useful crystallographic texts, for example, by Buerger (1956) and Phillips (1963*a*). General discussions of the theory associated with the applications of the group-theoretical studies of the point groups are given by many authors (for example; Bhagavantam and Venkatarayudu 1962, Cracknell 1968*b*, Hamermesh 1962, Heine 1960, Tinkham 1964).

We can also consider another collection of groups, this time by considering translational symmetry operations. If we were to look at the internal structure of a crystal we would find that it is made up of a large number of atoms or molecules regularly arranged; it would be possible to find a set of points within the crystal which are similar. That is, the crystal looks exactly the same if viewed from any one of these points as it does if it is viewed from any other of them. If we consider such a set of identical points they make up what the mathematicians call a *lattice*. It is possible to show that there is only a small number of essentially different ways of arranging a set of identical points so that the environment of each one is the same. This was done by Bravais (1850) who showed that in a three-dimensional space there are only

14 different lattices possible; consequently these are now known as *Bravais lattices*, even though Frankenheim had deduced, incorrectly, 15 such lattices somewhat earlier.

A point group is concerned with the symmetry of a finite object and for natural crystals there are only 32 different point groups; a Bravais lattice is concerned with the arrangement in space of a collection of mathematical points. To study fully the internal structure of a crystal, that is, the exact detailed arrangement of the atoms within the unit cell of a crystal, one needs a further development of symmetry studies known as a *space group*. A space group takes into consideration the symmetry of an arrangement of a set of identical objects, each of which is now not a point but is a finite object or a collection of atoms having some symmetry of its own. The actual operations present in a space group may be operations of the type which are present in point groups, namely pure rotations, reflections, the inversion operation, and roto-inversion or roto-reflection operations. But other operations are possible as well in a space group: they are screw rotation—and glide reflection operations—of symmetry. These are symmetry operations in which either a rotation axis or an ordinary reflection plane has a bodily movement of the crystal combined with it. In the descriptions of the derivation of the 230 space groups it is usually indicated that we owe them to Fedorov and Schönflies and sometimes the name of Barlow is added. A review of the history of the derivation of the space groups, together with a list of the publications of Barlow, Fedorov, and Schönflies, is given in an article by Burckhardt (1967). The derivation of the space groups has its origins in the works of Jordan (1868, 1869) and of Sohncke (1879). Sohncke had derived those space groups, of which there are 65, that contain only proper rotations and he noted that Jordan had previously derived them mathematically but had not translated his results into the more graphic terms of geometry. Schönflies re-derived these 65 space groups and extended the theory to include the space groups containing reflection planes of symmetry (Schönflies, 1887*a*, *b*, 1889, 1891). Similar results were derived by Fedorov (1885, 1891*a*) but his work was written in Russian and has not become so well known in western Europe; an account of the life and work of E. S. Fedorov and a list of his publications is given (in Russian) in the book by Shafranovskii (1963). It is evident that these two scientists began their works independently, one (Fedorov) as the director of a mine in the Urals and the other (Schönflies) at the suggestion of F. Klein at Göttingen, but in the course of time they heard of each other's work and compared their results. Barlow (1883) was first concerned with spherical packings and then starting with Sohncke's 65 groups he, too, obtained the remaining space groups by including reflection operations of symmetry (Barlow 1894). Burckhardt (1967) concludes that although Schönflies was not actually the first to establish the existence of the 230 space groups his writings have been the means of making their enumeration and identification generally known to the scientific world. His work, which is but little later than that of Fedorov and is quite independent, culminates in the book

Krystallsysteme und Krystallstructur (Schönflies 1891). A letter from Schönflies to Fedorov, quoted by Burckhardt (1967), reads 'I express my great joy about the agreement with your own views; I am particularly pleased, because I am no longer alone with my theory; it will still take great efforts before we shall succeed in winning over the crystallographers. *I concede you the priority with pleasure*, it is of no primary importance to me.' A convenient detailed list of the space groups in modern notation can be found in Volume 1 of the *International tables for X-ray crystallography* (Henry and Lonsdale 1965). At the present time there are about 9000 compounds whose space groups have been identified (for recent lists see Donnay, Donnay, Cox, Kennard, and King (1963), Nowacki, Edenharter, and Matsumoto (1967), and Wyckoff (1963, 1964, 1965, 1966, 1968)). The discovery of the two-dimensional space groups, which are also listed in detail in Volume 1 of the *International tables for X-ray crystallography*, is lost in the mists of antiquity because they arose in practice, in many different civilizations, in the designs of wallpapers or tiled floors (see, for example, Coxeter and Moser (1965), p. 33).

Although studies of a vast number of crystal structures had been undertaken by X-ray methods and these crystals had been assigned to the appropriate space groups, the study of the theory of symmetry seemed not to advance very much, after the derivation of the 230 space groups in about 1890, until Shubnikov in 1951 published a book called *Symmetry and anti-symmetry of finite figures* (in Russian, though this work is now translated into English, together with a list of many references to other works of Shubnikov (Shubnikov and Belov 1964)). A review of the developments in the theory of symmetry over the last 50 years is given by Koptsik (1967*a*) and a brief biography of A. V. Shubnikov is given at the beginning of volume 2 of *Kristallografiya* (*Soviet Phys. Crystallogr.* (English transl.) (1957)). The new developments were connected with introducing an operation of *anti-symmetry*. The classical theory of symmetry, point groups, Bravais lattices, and space groups, was essentially a 3-dimensional study, that is, a point P would be specified by the vector $\mathbf{r}\{=(x, y, z)\}$, and we would consider the effect of symmetry operations on this point. Shubnikov's basic idea was to say that in addition to the ordinary coordinates x, y, and z of a point we now also give each point a fourth coordinate, s, which can only take one of two possible values. The coordinate s can be the spin of a particle and the two allowed values will then correspond to spin up and spin down. Or, in purely abstract terms, they may be two colours such as black and white. If we include the coordinate s and if the values of s for the various atoms are randomly specified then the symmetry of the lattice has been completely destroyed. But if the spins are all parallel to a particular direction or if they are arranged in some regular fashion it is possible for some fraction of the symmetry to survive. If we introduce a new operation, which we may call the *operation of anti-symmetry*, $\mathscr{R}$, and consider this in conjunction with all the ordinary point-group and space-group operations it is possible to obtain a whole collection of new point groups and space groups which are called *black and white groups*, or *magnetic groups*, or *Shubnikov groups*. The idea of black and white groups was actually introduced long before Shubnikov's work, by Heesch (1929*a*, *b*, 1930*a*, *b*) and also discussed by Woods (1935*a–c*), but at that time there seemed to be no very great use for these groups in the description of physical systems. It was only with the introduction of the use of neutron diffraction techniques that it became apparent that these groups could be used in the description of magnetically ordered structures. If we think of s as being the two allowed values of a magnet's direction, parallel and anti-parallel to a particular direction, then $\mathscr{R}$ is the operation that reverses a magnetic moment. $\mathscr{R}$ can then be thought of as being the operation of *time-inversion*.

The theory of finite groups dates from the time of Cauchy‡ who was responsible for noticing that a number of apparently disconnected facts could be explained simultaneously by introducing the concept of a group. Galois§ added to the theory a number of new concepts, including that of an invariant subgroup, and part of his work on the theory of equations was a first and most startling example of the power of group theory in its applications. However, it is to Serret (1866) that we owe the first connected account of group theory. Since then there has been an increasing flow of literature on the subject and today abstract group theory still flourishes as a major topic for research. Furthermore, the variety of applications of finite groups in a host of mathematical situations as diverse as the theory of permutations, the study of symmetry, and the theories of algebraic and differential equations, to mention just a few, means that a study of groups is essential for those engaged in many disciplines requiring mathematical techniques. The natural sciences are riddled with examples of problems requiring a knowledge of group theory and it is a safe assumption that the biological sciences and perhaps even the social sciences, as they become increasingly mathematical, will produce further interesting applications.

In a mathematical theory it is often possible to pick out a number of famous scholars who have been responsible for the major advances. Group theory is no exception. The only fear we have in mentioning certain names is that those of many others who have made great advances are likely to be omitted. However, it is surely no injustice to single out the names of Sylow, Frobenius, Burnside, Schur, Miller, and Mackey (apologizing immediately to Noether, Brauer, Ito, and many others who have made great contributions to the theory of abstract groups but whose work is not so directly related to the applications in this book).

Sylow (1872) made considerable progress in describing the structure of a finite group particularly in relation to its number of elements when this number is factorized as a product of primes. Frobenius (1896*a*, *b*, 1898) originated and was largely responsible for the theory of group representations and group characters, though Burnside (1903, 1911) made such significant simplifications and was responsible for so many original results that he also must be thought of as a group theoretician of great influence.

‡ 1789–1857. § 1811–32.

As a worker with a prodigious output (of approximately 800 papers between 1894 and 1946) Miller (1894, 1946) devoted considerable attention to the investigation of the structures and properties of various groups of finite order. He was responsible for determining the numbers of finite groups of various specific orders and studying the interrelationships between the structures of these groups, as exemplified by their generating relations.

The study of relations between representations of a group and those of an invariant subgroup leads inevitably to projective representations. Schur was the first to notice this and in an astounding sequence of definitive papers (1904, 1907, 1911) he not only laid the foundations of the general theory of projective representations but established most of the results that are regarded as being of particular significance. Again it was Frobenius (1898) who was responsible for the first construction of what is now called an induced representation. However, this particular notion, so important to applications in physics, was not developed significantly until after 1950 when Mackey in a series of papers (1951, 1952, 1953*a*, *b*, 1958) made extremely important advances that already find considerable application not only in the theory of space groups but throughout the whole realm of theoretical physics (see also Mackey (1968)).

We have described the importance of point groups, Bravais lattices, and space groups in specifying both the macroscopic symmetry of a crystal, as determined by goniometry, and the symmetry of the internal structure of a crystal, as determined by X-ray diffraction or neutron diffraction experiments. In classical physics there are some applications of group theory, such as, for instance, the investigation of the normal modes of vibration of a molecule or solid (Wigner 1930) or the determination, for a crystal belonging to a given point group, of relationships that may exist between the various components of a tensor describing some macroscopic property (see, for example, Nye (1957)). However, it was with the advent of quantum mechanics that all the powerful mathematics of group theory and representation theory really became most useful in helping to understand physical systems. Much of the pioneer work on the application of group theory in quantum mechanics was done by Weyl, Wigner, and von Neumann (see Weyl (1931), the translation of the classic book by Wigner (1959) and the collected works of von Neumann (1961, 1963)). In studying a crystal at the microscopic level one has to remember that each of the individual particles of which the crystal is composed obeys quantum mechanics rather than classical mechanics and therefore has to be described by an appropriate wave function ψ. The key to the application of group theory to quantum mechanics lies in the result that is expounded in Chapter 11 of Wigner's classic book (English translation, Wigner (1959)). If a quantum-mechanical system is described by the appropriate Schrödinger wave equation Wigner's theorem can be summarized as follows: '*the representation of the group of the Schrödinger equation which belongs to a particular eigenvalue is uniquely determined up to a similarity transformation.*' Apart from accidental degeneracies this representation will be irreducible. The irreducible representations are therefore important because they can be used to label unambiguously the energy levels of a quantum-mechanical system. The irreducible representations of the crystallographic point groups and double point groups were determined a long time ago (Bethe 1929) and have been used extensively in labelling the energy levels of molecules (reviews and treatises include those of Eyring, Walter, and Kimball (1944), Nussbaum (1968), Rosenthal and Murphy (1936), Slater (1963), and Wilson, Decius, and Cross (1955)) in labelling the energy levels of ions or molecules in a crystal (reviews and discussions include those of Herzfeld and Meijer (1961), Hutchings (1964), Judd (1963), and McClure (1959*a*, *b*)) and also in labelling excitons in a crystal (Overhauser 1956). A particularly useful summary of the important properties of the crystallographic point groups and their representations is given by Koster, Dimmock, Wheeler, and Statz (1963).

The theory that underlies the determination of the irreducible representations of a space group was studied by Seitz (1936*b*) and first applied to symmorphic space groups by Bouckaert, Smoluchowski, and Wigner (1936), to non-symmorphic space groups by Herring (1942), and to double space groups by Elliott (1954*b*). Subsequently, many authors have determined the irreducible representations of individual space groups and, in doing so, have employed many different sets of notation. A substantial review was written by Koster (1957) and there have recently been published some sets of complete tables of the irreducible representations of all the 230 space groups (Faddeyev 1964, Kovalev 1965, Miller and Love 1967, Zak, Casher, Glück and Gur 1969). The importance of the irreducible representations of the space groups lies in the fact that, as a result of Wigner's theorem, they can be used in labelling the energy levels of a particle or quasi-particle in a crystal; they can therefore be used in labelling the electronic energy band structure and the phonon dispersion curves in a crystalline solid (for reviews see Blount (1962), Jones (1960), Nussbaum (1966), Slater (1965*b*, 1967) on electronic band structure, and Maradudin and Vosko (1968), Warren (1968) on phonon dispersion curves). Similarly, the irreducible representations of a space group can also be assigned to the magnon dispersion curves in a magnetic crystal. However, there is an added complication because the black and white Shubnikov space groups possess *corepresentations* rather than ordinary representations (Dimmock and Wheeler 1962*b*, Karavaev, Kudryavtseva, and Chaldyshev 1962, Loudon 1968, Wigner 1959, 1960*a*, *b*).

It is doubtful whether all the effort that workers have expended on the determination of point-group and space-group irreducible representations would be considered worth while if the only result was a scheme for labelling energy levels. However, the irreducible representations also enable one to determine the exact way in which a wave function ψ_i will transform under the various operations of the Schrödinger group of a molecule or crystal. This often enables some simplifications to be made when an unknown wave function is expanded in terms of a set of known functions such as spherical harmonics (Altmann 1957, Altmann and Bradley 1963*b*, Bell 1954, Betts

1959, McIntosh 1963, von der Lage and Bethe 1947) or plane waves (Cornwell 1969, Luehrmann 1968, Schlosser 1962, Slater 1965*b*, 1967). By restricting the expansion of an unknown ψ_i for an energy level E_i to those functions that are known to belong to the representation of E_i considerable simplifications can very often be achieved in the actual process of solving Schrödinger's equation to determine ψ_i. The knowledge of the transformation properties of the wave functions ψ_i is also of importance when considering a transition of a system between two energy levels E_i and E_j. It is then possible to use the condition that the quantum-mechanical matrix element of the transition is a pure number in order to determine, for any given perturbing potential, whether a given transition is allowed or forbidden, that is, to determine *selection rules*. The group-theoretical determination of selection rules for transitions in isolated molecules and in ions or molecules in crystals involves the study of products of various point-group representations and this is discussed in the references we have already mentioned. To use the knowledge of the transformation properties of ψ_i to study selection rules for transitions involving non-localized states in crystals is more complicated and initial work has been done by several authors (Birman 1962*b*, 1963, Elliott and Loudon 1960, Lax and Hopfield 1961, Zak 1962).

1.2. Group theory

We begin the mathematical work of this book by giving a short account of the theory of groups and their representations. We do not give proofs of theorems as these appear in the first few chapters of many well-known books such as those by Hamermesh (1962), Lomont (1959), Lyubarskii (1960), and Wigner (1959). For the sake of clarity, however, we illustrate some of the definitions and theorems by means of an example; for this purpose we use a group containing six elements which, as an abstract group we call $\mathbf{G}_6^2$ (see Table 5.1) and which, in one of its realizations, is the symmetry group of an equilateral triangle.

There are two good reasons for starting with a preliminary account such as this. The first is that it makes clear what the background to the work is, and hence what it is recommended that the reader should be familiar with before proceeding with the rest of the book. The second reason is that it serves to introduce a large amount of notation; furthermore, when this is done on topics that are relatively familiar, then a reader can adjust himself more easily to the style and notation of the authors than if he is plunged immediately into new work.

The following set of definitions and theorems forms, therefore, the group-theoretical background to the work of this book. In later chapters some of them will be used as building blocks for further theorems that are either more advanced or more directly related to the study of solids. The groups that occur in the theory of solids have quite a complicated structure and, if the theorems needed for dealing with them are established rigorously and in complete detail, the proofs of such theorems require some advanced algebraic methods not commonly met in introductory courses on