

PHONONS AND RESONANCES IN SOLIDS

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PREFACE

The purpose of this book is to present a treatment of the thermal vibrations of crystalline solids and of their effects on the spectra of these materials. Crystalline solids present spectra whose frequency distribution reflects the structure of their energy levels. This structure becomes manifest in absorption spectra every time the frequency of the incoming light is in "resonance" with one of the energy levels of the system; in emission, the spectral distribution also reflects the energy spacings of the system. It is also possible to derive spectral information by using scattering experiments where the incoming photon or neutron, by passing through the system, experiences a variation of its energy in accordance with a quantum of excitation in the solid.

In general, the energy levels of a solid may arise from a collective excitation of all the atoms or from localized centers; also, they can be determined mainly by the electrons or by the thermal vibrations of the atoms. In general, excitations of different types (say, electronic or vibrational) occur in different spectral regions, so that they may be studied separately; in some other cases, for example, in the case of vibronic transitions, both electronic and vibrational excitation play a role in the radiative process.

In order to study the spectrum of a solid the researcher uses probes (like a beam of light, a beam of neutrons) that interact with the constituents of the crystal. Experimental investigations may be directly pointing to the measurement of vibrations using such varied techniques as infrared absorption, Raman and Brillouin scattering, and neutron scattering. Other experiments may deal with optical spectra, and be strongly affected by the presence of thermal vibrations (to the point that they may even provide some relevant information about these vibrations).

In other words, a researcher may face two different types of problems:

1. He makes the thermal vibrations the object of his study. He uses spectroscopic techniques to investigate the phonon spectrum of the solid.
2. He wants to understand how thermal vibrations affect his results.

This book is addressed to both types of approaches to the research in this field and may be of great interest not only to researchers in the field of solid-state spectroscopy but also to students and teachers of solid-state physics.

There are, of course, other thermal effects in solids that are not closely related to spectral data and will not be treated here. For example, thermal transport properties and interaction of phonons with charge carriers in metals and semiconductors are two areas that have been the subject of extensive investigation and have already been treated in detail in the literature.

The present treatment proceeds along the following lines:

1. The Introduction (Chapter I) sets the stage for the entire book by treating the Hamiltonian of a crystalline solid, introducing the adiabatic approximation, and considering the consequences of this approximation on the role that symmetry plays.
2. Since solids are ordered arrays of atoms, their symmetry properties are intimately related to their physical properties. A study of the symmetries of crystals is then essential for an understanding of their properties, in particular of their spectra. This study is carried out in Chapters 2-4.
3. The thermal vibrations of a solid are the next subject of this study. Both their theoretical treatment (Chapters 5 and 6) and some of the experimental techniques used to investigate them (Chapters 7 and 8) are considered.
4. The next subject of this study is the interaction of radiation with matter (Chapter 9), which produces optical spectra in the presence of impurities (Chapters 10 and 11) or infrared absorption and Raman Scattering (Chapter 12), when the radiation interacts with the vibrations of that solid.

The content of this book could be the subject of a two-term graduate course on solid-state physics. It presupposes the equivalent of one year of study of quantum mechanics. Although group theory is used throughout the book, no previous knowledge of this subject is required.

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CONTENTS

1. INTRODUCTION	1
1.1 The Hamiltonian of a Crystalline Solid, 1	
1.2 The Adiabatic Approximation, 4	
1.3 The Role of Symmetry, 5	
1.4 The Symmetries of the Hamiltonian, 6	
Reference, 9	
2. CONCEPTS OF GROUP THEORY	10
2.1 Properties of a Group, 10	
2.2 Subgroups, Cosets, and Classes, 12	
2.3 Theory of Representations, 15	
2.4 Orthogonality Relations, 18	
2.5 Characters of a Matrix Representation, 21	
2.6 Reduction of a Reducible Representation, 23	
2.7 Basis Functions for Irreducible Representations, 25	
2.8 Direct Product Representations, 27	
2.9 The Fundamental Theorem for Functions Transforming Irreducibly, 28	
2.10 Product Groups and Their Representations, 32	
2.11 Connections of Quantum Mechanics with Group Theory, 33	
3. CRYSTAL SYMMETRIES	38
3.1 Unit Cells and Space Lattices, 38	
3.2 Miller Indices, 40	
3.3 The Crystal Systems, 45	
3.3.1 The Four Two-Dimensional Crystal Systems, 45	
3.3.2 The Seven Three-Dimensional Crystal Systems, 45	
3.4 The Bravais Lattices, 48	
3.4.1 The Five Bravais Lattices in Two Dimensions, 48	
3.4.2 The Fourteen Bravais Lattices in Three Dimensions, 50	

4. GROUP-THEORETICAL TREATMENT OF CRYSTAL SYMMETRIES	57
4.1 Space Groups, 57	
4.2 The Crystallographic Point Groups, 60	
4.2.1 Two-Dimensional Crystallographic Point Groups, 60	
4.2.2 Three-Dimensional Crystallographic Point Groups, 61	
4.2.3 Site Groups, 65	
4.3 The Invariant Subgroup of Primitive Translations: Bravais Lattices, 68	
4.4 The Compatibility of Rotational and Translational Symmetries and Its Relevance to Space Groups, 70	
4.5 The Irreducible Representations of a Group of Primitive Translations. Brillouin Zones, 75	
4.6 The Irreducible Representations of Space Groups, 81	
4.6.1 Effects of Translational Symmetry, 81	
4.6.2 Effects of Rotational Symmetry, 82	
4.6.3 General Properties of the Irreducible Representations, 84	
4.6.4 Small Representations for Different Points of the Brillouin Zone, 87	
4.7 Example I. Symmorphic Group C_{4v}^1 , 90	
4.8 Example II. Nonsymmorphic Group C_{4v}^2 , 113	
References, 137	
5. LATTICE VIBRATIONS	138
5.1 The Infinite Linear Crystal, 138	
5.2 The Finite Linear Crystal, 143	
5.3 Normal Modes of Vibration of a Linear Crystal, 147	
5.4 Linear Crystal with a Basis, 156	
5.5 Lattice Vibrations in Three Dimensions, 165	
5.5.1 The Equations of Motion, 165	
5.5.2 Allowed Values of k . Density of Phonon Modes, 167	
5.5.3 Normal Modes of Vibration, 171	
5.5.4 Energy Levels, 176	
5.5.5 Particular Modes of Vibration, 180	
5.5.6 Spectrum of Lattice Vibrations, 182	
5.6 Group Theory and Lattice Vibrations, 184	
5.6.1 Properties of the Normal Coordinates, 184	
5.6.2 The Frequency Eigenvalues and the Polarization Vectors, 185	
5.6.3 Additional Degeneracies Not Due to Spacelike Symmetries, 189	
5.6.4 Time-Reversal Degeneracy, 191	

- 5.7 Group Theoretical Analysis of the Lattice Vibrations of a Linear Crystal, 194
 - 5.7.1 Case of One Atom per Unit Cell, 194
 - 5.7.2 Case of Two Atoms per Unit Cell, 200
- 5.8 Group-Theoretical Analysis of the Lattice Vibrations of a Three-Dimensional Crystal, 203
- 5.9 Example I. Lattice Vibrations of a Two-Dimensional Crystal with Symmetry C_{4v}^1 , 207
- 5.10 Example II. Lattice Vibrations of a Two-Dimensional Crystal with Symmetry C_{4v}^2 , 216
- References, 229

6. THERMODYNAMICS OF LATTICE VIBRATIONS 230

- 6.1 Thermodynamics of Specific Heats, 230
- 6.2 The Classical Theory of the Specific Heats of Solids, 232
- 6.3 The Einstein Theory of Specific Heat, 233
- 6.4 The Debye Theory of Specific Heat, 237
 - 6.4.1 The Specific Heat of a Linear Crystal, 237
 - 6.4.2 The Debye Theory Applied to a Linear Crystal, 241
 - 6.4.3 The Debye Theory Applied to a Three-Dimensional Crystal, 243
- 6.5 Temperature Dependence of the Amplitude of Vibrations in Solids. The Lindemann Law of Melting, 252
- References, 256

7. SCATTERING OF X-RAYS BY CRYSTALS 257

- 7.1 Introduction, 257
- 7.2 Scattering from a Single Electron, 258
- 7.3 Scattering from a Single Atom, 262
- 7.4 Scattering from the Atoms in the Unit Cell of a Crystal, 264
- 7.5 Scattering from a Crystal, 265
- 7.6 Interpretation of Laue Equations in Reciprocal Space, 270
- 7.7 Methods of X-Ray Diffraction, 273
 - 7.7.1 The Laue Method, 273
 - 7.7.2 The Bragg Method, 275
 - 7.7.3 The Debye-Scherrer Method, 275
- 7.8 Effect of Thermal Vibrations on the Intensity of Scattered Radiation, 275
 - 7.8.1 The Intensity of the Scattered Radiation, 275

7.8.2	<i>The Effect of Lattice Vibrations: Einstein Model,</i>	
	276	
7.8.3	<i>The Effect of Lattice Vibrations: Normal Mode</i>	
	<i>Treatment, 280</i>	
	References, 288	
8.	SCATTERING OF NEUTRONS BY CRYSTALS	289
8.1	Introduction, 289	
8.2	Theory of Neutron Scattering, 291	
8.3	Elastic Neutron Scattering, 296	
8.4	Inelastic Neutron Scattering, 300	
8.5	Application of Neutron Scattering to the Study of Lattice	
	Vibrations, 306	
	References, 310	
9.	INTERACTION OF RADIATION WITH MATTER	311
9.1	The Classical Radiative Field, 311	
9.2	The Quantum Theory of the Radiative Field, 321	
9.3	The Hamiltonian of a Charged Particle in an Electromag-	
	netic Field, 323	
9.4	The Interaction Between a Charged Particle and a Radia-	
	tive Field, 325	
9.5	First-Order Processes. Absorption and Emission of	
	Radiation, 328	
9.6	Second-Order Processes, 336	
9.6.1	Matrix Elements Due to H_1 , 337	
9.6.2	Matrix Elements Due to H_2 , 339	
9.6.3	Effective Matrix Element, 339	
9.6.4	Transition Rates of Scattering Processes, 344	
	References, 346	
10.	OPTICAL SPECTRA OF IMPURITIES IN SOLIDS. I	348
10.1	Impurities in Crystals, 348	
10.2	Review of the Theory of Small Vibrations (Classical),	
	349	
10.3	Harmonic and Anharmonic Relaxation, 359	
10.4	Review of the Theory of Small Vibrations (Quantum	
	Mechanical), 362	
10.5	The Effect of Impurities on Lattice Vibrations, 368	
10.6	The Franck-Condon Principle, 373	

10.7	Absorption and Emission in Crystals, 381	
10.8	Purely Electronic (Zero-Phonon) Transitions, 384	
10.9	Characteristics of Zero-Phonon Lines, 394	
10.10	Phonon-Assisted Transitions, 396	
10.11	Radiative Transitions in the Presence of Localized Vibrations, 404	
10.12	Classification of Vibronic Spectra, 414	
	References, 415	
11.	OPTICAL SPECTRA OF IMPURITIES IN SOLIDS, II	417
11.1	Summary of Previous Results, 417	
11.2	Deviations from the Franck-Condon Approximation, 420	
11.3	Deviations from the Adiabatic Approximation. Radiationless Transitions, 436	
11.4	A Simple Model for Laser Crystals: An Effective Hamiltonian, 439	
11.5	Radiative, Vibronic, and Radiationless Transitions of Magnetic Impurities, 442	
11.6	Selection Rules for Vibronic Transitions, 452	
11.7	Effect of Temperature on the Position and Shape of a Purely Electronic Line, 454	
	11.7.1 Thermal Line Shift, 454	
	11.7.2 Thermal Broadening of Sharp Lines, 456	
	References, 459	
12.	INTERACTION OF LIGHT WITH LATTICE VIBRATIONS: INFRARED ABSORPTION AND RAMAN SCATTERING	461
12.1	General Characteristics of Infrared Absorption by Crystals, 461	
12.2	Infrared Transitions in a Molecular System, 462	
12.3	Momentum and Energy Conservation in Infrared Absorption, 463	
12.4	Quantum Theory of Infrared Absorption, 467	
12.5	Reststrahl (One-Phonon) Absorption, 476	
12.6	Two-Phonon Absorption, 480	
12.7	Selection Rules for Infrared Absorption, 485	
12.8	The Effect of Impurities on Infrared Absorption Spectra, 487	
12.9	General Characteristics of Raman Scattering from Crystals, 488	
12.10	Theory of Raman Scattering, 490	
12.11	Transition Polarizability, 495	

xvi Contents

- 12.12 Energy Scattered in Raman Scattering Experiments, 500
- 12.13 Selection Rules for Raman Scattering, 504
- 12.14 The Effect of Impurities on Raman Scattering, 507
References, 507

AUTHOR INDEX 511

SUBJECT INDEX 513

1

INTRODUCTION

1.1 THE HAMILTONIAN OF A CRYSTALLINE SOLID

A crystalline solid is an ordered array of atoms bound together. The Hamiltonian of such a system that includes n electrons and N nuclei is given by

$$H = \sum_{i=1}^n \frac{p_i^2}{2m} + \sum_{\alpha=1}^N \frac{P_{\alpha}^2}{2M_{\alpha}} + V(r_i, R_{\alpha}) \quad (1.1.1)$$

where m is the mass of the electron, M_{α} is the mass of the α th nucleus, r_i is the position coordinate of the i th electron, p_i is the linear momentum of the i th electron, R_{α} is the position coordinate of the α th nucleus, and P_{α} is the linear momentum of the α th nucleus. Also

$$V(r_i, R_{\alpha}) = V_{ee} + V_{nn} + V_{ne} \quad (1.1.2)$$

where

$$V_{ee} = \frac{1}{2} \sum_{i=1}^n \sum_{j \neq i}^n \frac{e^2}{|r_i - r_j|}$$

$$V_{nn} = \frac{1}{2} \sum_{\alpha=1}^N \sum_{\beta \neq \alpha}^N \frac{e^2 Z_{\alpha} Z_{\beta}}{|R_{\alpha} - R_{\beta}|}$$

$$V_{ne} = - \sum_{i=1}^n \sum_{\alpha=1}^N \frac{e^2 Z_{\alpha}}{|R_{\alpha} - r_i|}$$

2 Introduction

The Schrödinger equation of the system is given by

$$H\Psi(\underline{r}_i, \underline{R}_\alpha) = E\Psi(\underline{r}_i, \underline{R}_\alpha) \quad (1.1.3)$$

where the Hamiltonian operator H is expressed as follows:

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 - \frac{\hbar^2}{2} \sum_{\alpha=1}^N \frac{\nabla_\alpha^2}{M_\alpha} + V(\underline{r}_i, \underline{R}_\alpha) \quad (1.1.4)$$

Therefore the eigenfunctions and the eigenvalues of the system are given by

$$-\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 \Psi - \frac{\hbar^2}{2} \sum_{\alpha=1}^N \frac{1}{M_\alpha} \nabla_\alpha^2 \Psi + V\Psi = E\Psi \quad (1.1.5)$$

In order to solve the above Schrödinger equation we seek solutions of the type

$$\Psi(\underline{r}_i, \underline{R}_\alpha) = \phi(\underline{R}_\alpha) \psi(\underline{r}_i, \underline{R}_\alpha) \quad (1.1.6)$$

Using (1.1.6) in (1.1.5) we obtain, dropping the subscripts i and α ,

$$\begin{aligned} & -\frac{\hbar^2}{2m} \phi(\underline{R}) \sum_{i=1}^n \nabla_i^2 \psi(\underline{r}, \underline{R}) - \frac{\hbar^2}{2} \sum_{\alpha=1}^N \frac{\nabla_\alpha^2}{M_\alpha} \phi(\underline{R}) \psi(\underline{r}, \underline{R}) \\ & + V(\underline{r}, \underline{R}) \phi(\underline{R}) \psi(\underline{r}, \underline{R}) = E\phi(\underline{R}) \psi(\underline{r}, \underline{R}) \end{aligned} \quad (1.1.7)$$

But

$$\begin{aligned} \nabla_\alpha^2 \phi(\underline{R}) \psi(\underline{r}, \underline{R}) &= \phi(\underline{R}) \nabla_\alpha^2 \psi(\underline{r}, \underline{R}) + \psi(\underline{r}, \underline{R}) \nabla_\alpha^2 \phi(\underline{R}) \\ &+ 2\nabla_\alpha \phi(\underline{R}) \cdot \nabla_\alpha \psi(\underline{r}, \underline{R}) \end{aligned} \quad (1.1.8)$$

Then

$$\begin{aligned} & -\sum_{\alpha=1}^N \frac{\hbar^2}{M_\alpha} \nabla_\alpha \phi(\underline{R}) \cdot \nabla_\alpha \psi(\underline{r}, \underline{R}) - \sum_{\alpha=1}^N \frac{\hbar^2}{2M_\alpha} \phi(\underline{R}) \nabla_\alpha^2 \psi(\underline{r}, \underline{R}) \\ & - \psi(\underline{r}, \underline{R}) \sum_{\alpha=1}^N \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 \phi(\underline{R}) - \phi(\underline{R}) \sum_{i=1}^n \frac{\hbar^2}{2m} \nabla_i^2 \psi(\underline{r}, \underline{R}) \\ & + V(\underline{r}, \underline{R}) \phi(\underline{R}) \psi(\underline{r}, \underline{R}) = E\phi(\underline{R}) \psi(\underline{r}, \underline{R}) \end{aligned} \quad (1.1.9)$$

1.1 The Hamiltonian of a Crystalline Solid 3

We will assume that

$$\left| -\sum_{\alpha=1}^N \frac{\hbar^2}{M_{\alpha}} \left[\nabla_{\alpha} \phi \cdot \nabla_{\alpha} \psi + \frac{1}{2} \phi \nabla_{\alpha}^2 \psi \right] \right| \ll \left| -\psi \sum_{\alpha=1}^N \frac{\hbar^2}{2M_{\alpha}} \nabla_{\alpha}^2 \phi \right| \quad (1.1.10)$$

We shall return to the validity of this assumption later. Because of (1.1.10), (1.1.9) becomes

$$-\frac{\hbar^2}{2} \frac{\psi}{\phi} \sum_{\alpha=1}^N \frac{1}{M_{\alpha}} \nabla_{\alpha}^2 \phi + \left[-\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 + V(\underline{r}, \underline{R}) \right] \psi = E\psi. \quad (1.1.11)$$

The operator in the square brackets on the left-hand side of (1.1.11) represents the Hamiltonian for the system if the nuclei are assumed to be fixed in space. We call this Hamiltonian H_e :

$$H_e = -\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 + V(\underline{r}, \underline{R}) \quad (1.1.12)$$

The corresponding eigenfunctions and eigenvalues are given by the Schrödinger equation,

$$-\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 \psi(\underline{r}, \underline{R}) + V(\underline{r}, \underline{R}) \psi(\underline{r}, \underline{R}) = \epsilon(\underline{R}) \psi(\underline{r}, \underline{R}) \quad (1.1.13)$$

Replacing (1.1.13) in (1.1.11) we obtain

$$-\frac{\hbar^2}{2} \sum_{\alpha=1}^N \frac{1}{M_{\alpha}} \nabla_{\alpha}^2 \phi(\underline{R}) + \epsilon(\underline{R}) \phi(\underline{R}) = E\phi(\underline{R}) \quad (1.1.14)$$

The solution of the Schrödinger equation (1.1.3) reduces then to the solution of the two equations (1.1.13) and (1.1.14); we now rewrite this solution with the proper subscripts as follows:

$$-\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 \psi_k(\underline{r}, \underline{R}) + V(\underline{r}, \underline{R}) \psi_k(\underline{r}, \underline{R}) = \epsilon_k(\underline{R}) \psi_k(\underline{r}, \underline{R}) \quad (1.1.15)$$

$$-\frac{\hbar^2}{2} \sum_{\alpha=1}^N \frac{1}{M_{\alpha}} \nabla_{\alpha}^2 \phi_{kl}(\underline{R}) + \epsilon_k(\underline{R}) \phi_{kl}(\underline{R}) = E_{kl} \phi_{kl}(\underline{R}) \quad (1.1.16)$$

A stationary state of the system will be represented by the eigenfunction

$$\Psi_n(\underline{r}, \underline{R}) = \psi_k(\underline{r}, \underline{R}) \phi_{kl}(\underline{R}) \quad (1.1.17)$$

4 Introduction

where $\psi_k(\underline{r}, \underline{R})$ and $\phi_{k1}(\underline{R})$ are eigenfunctions of the Hamiltonians

$$H_e = -\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 + V(\underline{r}, \underline{R}) \quad (1.1.18)$$

and

$$H_v = -\frac{\hbar^2}{2} \sum_{\alpha=1}^N \frac{\nabla_{\alpha}^2}{M_{\alpha}} + \epsilon_k(\underline{R}), \quad (1.1.19)$$

respectively.

1.2 THE ADIABATIC APPROXIMATION

Let us consider now in detail equations (1.1.15) and (1.1.16). Equation (1.1.15) is an eigenvalue equation whose eigenfunctions represent the motion of the electrons in the crystal when the nuclei are kept fixed in space. The energy eigenvalues of (1.1.15) depend parametrically on the nuclear coordinates. Equation (1.1.16) is an eigenvalue equation whose eigenfunctions represent the motion of the nuclei in the crystal. In the Hamiltonian (1.1.19) for nuclear motion, the energy $\epsilon_k(\underline{R})$, which is a function of the nuclear coordinates regarded as parameters, plays the role of the potential energy for nuclear motion. This potential energy $\epsilon_k(\underline{R})$ is an eigenvalue of (1.1.15) and, as such, depends on the quantum number k . The eigenfunction $\phi(\underline{R})$ also depends on k ; however, k does not play the role of a quantum number for $\phi(\underline{R})$ even if it is used as one of its subscripts. Therefore the functions $\phi_{k1}(\underline{R})$ and $\phi_{k'1}(\underline{R})$ with $k' \neq k$ are not mutually orthogonal.

We now return to the approximation (1.1.10) and discuss its physical meaning. The implication of (1.1.10) is that the function $\psi(\underline{r}, \underline{R})$, which represents the motion of the electrons, is a function that varies slowly with the nuclear coordinates, so that $|\nabla_{\alpha} \psi(\underline{r}, \underline{R})|$ is much smaller than $|\nabla_{\alpha} \phi(\underline{R})|$. In pictorial terms we may say that this is the case since the electrons, having much smaller masses than the nuclei, go through their orbits many times before the nuclei have shifted from their equilibrium position by any considerable distance.

In the light of this fact the approximation (1.1.10), which has allowed us to express the eigenstates of the system in the product form (1.1.6), is called the *adiabatic approximation*. It is also called sometimes the *Born-Oppenheimer approximation*.¹

The implications of the adiabatic approximation are far reaching. We are now in the position of treating the electrons and the nuclei independently; we will, however, keep in mind that we are allowed to do so only within the limits of validity of the adiabatic approximation.

1.3 THE ROLE OF SYMMETRY

The quantum-mechanical treatment of a physical system implies generally the solution of a Schrödinger equation. This solution gives the energy eigenvalues and the eigenfunctions of the Hamiltonian. In general the eigenfunctions are degenerate; that is, several of them correspond to the same energy eigenvalue. The degeneracy and the transformation properties of the eigenfunctions are closely related to the symmetry properties of the Hamiltonian; indeed, both degeneracy and transformation properties can be derived from the knowledge of symmetries.

Before considering these symmetries for the case of a crystalline solid, it is worthwhile to review some basic concepts regarding coordinate transformations. In particular we are concerned with those transformations that leave the distance between two points unchanged. The most general transformation of this type can be expressed by the symbol $\{R|\underline{t}\}$ and involves a rotational operation R followed by a translation \underline{t} . A position vector \underline{x} , when acted upon by $\{R|\underline{t}\}$, becomes

$$\underline{x}' = R \underline{x} + \underline{t} \quad (1.3.1)$$

with

$$\begin{aligned} x'_1 &= R_{11}x_1 + R_{12}x_2 + R_{13}x_3 + t_1 \\ x'_2 &= R_{21}x_1 + R_{22}x_2 + R_{23}x_3 + t_2 \\ x'_3 &= R_{31}x_1 + R_{32}x_2 + R_{33}x_3 + t_3 \end{aligned} \quad (1.3.2)$$

R is a 3×3 real orthogonal matrix: if its determinant is $+1$, the rotation is called *proper*; if its determinant is -1 , the rotation is called *improper*.

A pure rotation is indicated by $\{R|0\}$ and a pure translation by $\{E|\underline{t}\}$. The identity operation is represented by $\{E|0\}$.

If two operations $\{R_1|\underline{t}'\}$ and $\{R_2|\underline{t}''\}$ act in succession upon a vector \underline{x} , the result is

$$\underline{x}' = R_1 \underline{x} + \underline{t}' \quad (1.3.3)$$