Functional Cobalt Oxides

FUNDAMENTALS, PROPERTIES, AND APPLICATIONS

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PAN STANFORD PUBLISHING

Published by

Pan Stanford Publishing Pte. Ltd.
Penthouse Level, Suntec Tower 3
8 Temasek Boulevard
Singapore 038988

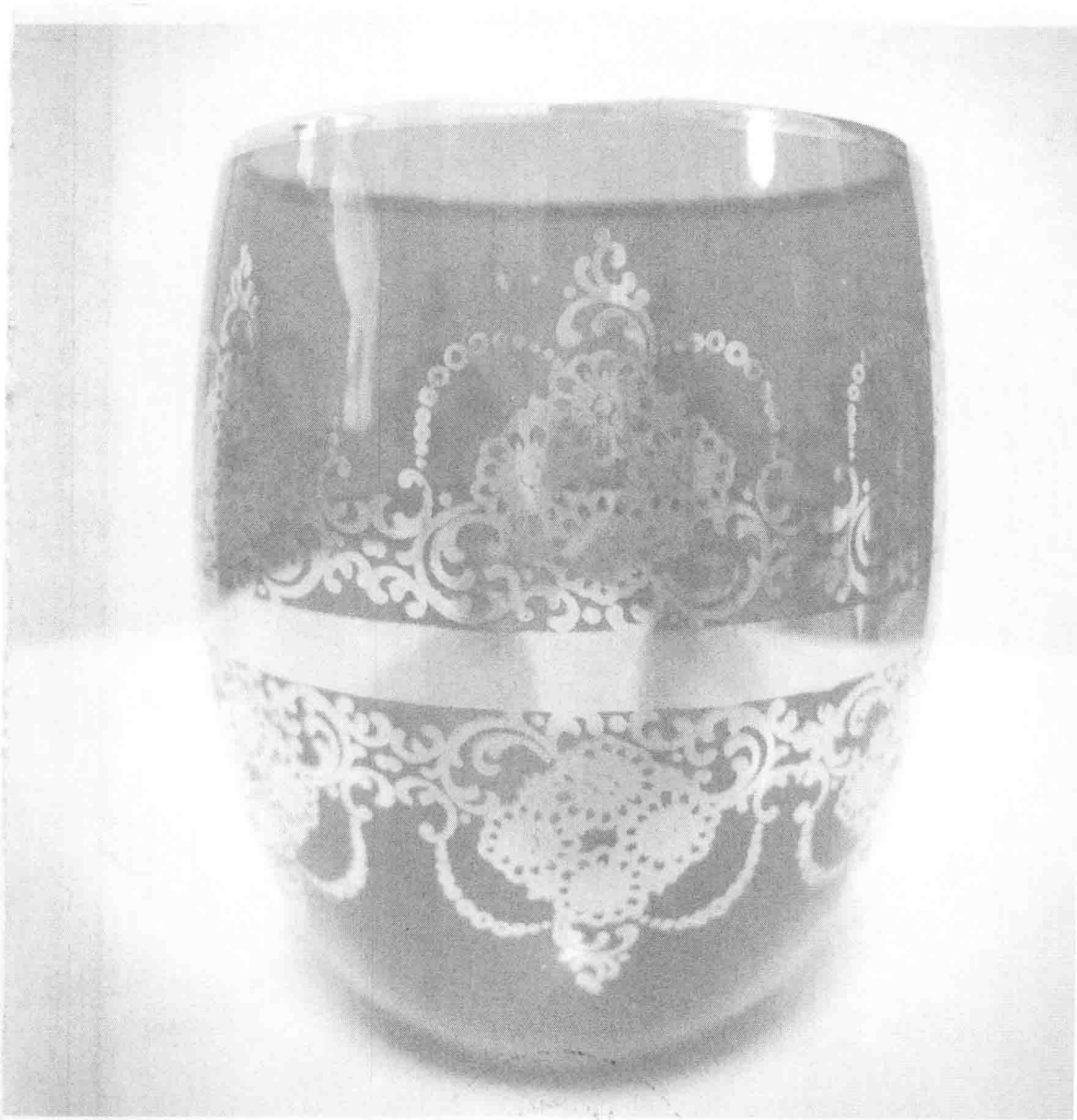
Email: editorial@panstanford.com
Web: www.panstanford.com

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Functional Cobalt Oxides: Fundamentals, Properties, and Applications

ISBN 978-981-4463-32-4 (Hardcover)
ISBN 978-981-4463-33-1 (eBook)

Printed in the USA



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Preface

When one looks around, one's apparels are found to made of many materials, which are said to reach 50,000 varieties. Surprisingly, these materials are composed of at most about 50 kinds of elements. Among them, the transition metals have a high melting point, high density, and multivalence. This book deals with oxide materials, including the transition metal Co, but the elementary Co itself with the 29th Clarke number exhibits ferromagnetism, as well as Ni and Fe, and has been used as a dye and a pigment to produce the well-known cobalt blue. There is a view according to which Co was designated by H. Brandt in 1735, and its name stems from German word "*Kobold*." In this connection, I may add that the name appears in a worldwide animation, *Mightly Atom*, created by O. Tezuka, as the name of the brother of the main character, Atom. Moreover, Co has been also widely used as alloys with Fe, Ni, and Cr: Ni-Fe-Co alloy is employed as a binder between glass and metal and Cr-Co-W alloy is dental or surgery material.

The book is motivated by the desire to describe why cobalt oxides have drawn much interest as functional materials, together with their peculiar physical properties partially originating from a rich variety of valences and spin states of Co ions. The leading role of the physical phenomena dealt with in this book is owed to the electron. The electron, discovered by J. J. Thomson in 1897, is a particle that cannot be far resolved under normal conditions and has a wave nature as well. Wave-particle duality was evidenced by experiments using the double split performed by C. Jönsson, P. G. Merli, and A. Tonomura in 1961, 1974, and 1989, respectively.

In the Co oxide system, the strong correlation between electrons generally plays a substantial role, where the conventional one-electron approximation fails. In particular, the characteristics of

Co ions in oxides should be focused on in comparison with other transition metals. This book starts with the basis of one-electron band theory and advances toward the stage of strong electron correlation systems and furthermore progresses to cover up-to-date topics such as huge thermoelectric power, superconductivity, and intrinsic inhomogeneity, etc. This book would be of interest to graduate students and researchers in the fields of physics, chemistry, and materials science. Aside from helping readers in the pencil-and-paper solution of problems, the discussion, which this book aims at developing, may be useful for understanding the essence of functional materials.

Tsuyoshi Takami

Acknowledgments

I acknowledge support from the Foundation of a Grant-in-Aid for Young Scientists (B) (Grant No. 21740251 and No. 24740233), Ando Laboratory, Thermal & Electric Energy Technology Foundation, Japan Society for the Promotion of Science (JSPS) Research Fellowships for Young Scientists, the Sasakawa Scientific Research Grant from the Japan Science Society, and the Research Foundation for the Electrotechnology of Chubu. It's thanks to Emeritus Prof. Uichiro Mizutani, Prof. Hiroshi Ikuta, and Dr. Jun Sugiyama that our achievements were successfully obtained and became worthy to be published as this book. Furthermore, I appreciate Profs. Tsunehiro Takeuchi, Jinguang Cheng, and Masayuki Itoh and Dr. Hiroshi Nozaki for their collaboration. Profs. John B. Goodenough and Jianshi Zhou are also thanked for useful discussions. I am indebted to Mr. Sarabjeet Garcha, senior editorial manager of Pan Stanford Publishing Pte. Ltd., for his advice on form and assistance for preparation. I appreciate Mr. Stanford Chong, director and publisher of Pan Stanford Publishing Pte. Ltd., for inviting me to develop my research topic into this book.

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Chapter 1

Introduction

1.1 Prologue

Cobalt oxides are known to exhibit peculiar physical/chemical properties, as well as being suitable candidates for wide applications such as electrode materials, thermoelectric materials, solid oxide fuel cells, and so forth. Such properties are closely related to versatility of the cobalt cations to adopt different valences and spin states in the narrow energy range, which associate with the charge and spin configuration on $3d$ orbitals, respectively. In this chapter, the charge, spin, and orbital for the $3d$ electron system are introduced, and then their role in the transport properties under external perturbations is formulated.

1.2 Charge, Spin, and Orbitals

Since electrons in materials are attracted by an atomic nucleus, their characteristics depend on the kind of elements and orbitals. The elements generally show the tendency given in Table 1.1. The density of conduction electrons $\rho(r)$ at a distance r from a certain atom deviates from the initial $\rho_0(r)$, and the potential $\varphi(r)$ and $\rho(r)$

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Table 1.1 Characteristics of representative elements

	Alkaline metal	Transition metal	Actinoid metal	Rare-earth metal
Orbital	s	$3d$	$5f$	$4f$
Element	K, Na, ···	Fe, Co, ···	Pa, U, ···	Ce, Pr, ···
Extension of the wave function	large	middle	middle	small
Characteristic	itinerant	itinerant/localized	itinerant	localized
Electron correlation	weak	strong	midrange	strong

are connected with the Poisson equation:

$$\nabla^2\varphi = -4\pi e^2\rho(r) - \rho_0(r). \tag{1.1}$$

The proportional relationship of $(2\pi/L)^3 : 2 = 4\pi k_F^3/3 : N_A$ leads to

$$k_F = 3\pi^2(N_A/V)^{1/3} = (3\pi^2\rho(r))^{1/3}, \tag{1.2}$$

where L, k_F, N_A, and V are the edge length, the radius of the Fermi sphere, the Avogadro number, and the volume, respectively. Thus,

$$E_F + \varphi(r) = \left(\frac{\hbar}{2m}\right)(3\pi^2\rho(r))^{2/3} \tag{1.3}$$

holds, which is converted to

$$\rho(r) = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar}\right)^{3/2} E_F^{3/2}\left(1 + \frac{\varphi}{E_F}\right)^{3/2}, \tag{1.4}$$

where E_F and $\hbar$ are the Fermi energy and the Planck's constant, respectively. By applying the Taylor expansion, this equation can be written as

$$\rho(r) = \rho_0\left(1 + \frac{3}{2}\frac{\varphi}{E_F}\right), \tag{1.5}$$

where $\rho_0 = (1/3\pi^2)(2m/\hbar^2)^{3/2}E_F^{3/2}$.

Insertion into Eq. 1.1 gives

$$\nabla^2\varphi = -\lambda^2\varphi, \tag{1.6}$$

where $\lambda = (6\pi e^2\rho_0/E_F)^{1/2}$. This equation is a function of the radius parameter r in the spherical coordinate and is rewritten as

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\varphi(r)}{dr}\right) = \lambda^2\varphi(r), \tag{1.7}$$

and thus it can be confirmed that its solution becomes

$$\varphi(r) = -\frac{e^2 \Delta Z \exp(\lambda r)}{r^2}, \tag{1.8}$$

where ΔZ is the difference of the amount of charge. The parameter λ is called the Thomas–Fermi screening parameter. For instance, for the Co element alone, the insertion of $E_F = 7.4$ eV and $\rho_0 = 9.1 \times 10^{22}$ /cm^3 gives $1/\lambda = 0.55$ Å. On the other hand, the intratomic distance equals the lattice constant a of 2.51 Å. Consequently, one can realize how effective the screening effect is because of $1/\lambda \ll a$.

For strongly correlated electron systems, since the scattering effect is less effective, three internal degrees of freedom of electrons, that is, charge, spin, and orbital, can be attributable to physical properties, which cannot be explained by a conventional band picture. When such degeneracies functionate on the crystal lattice, various electronic phases are formed. Charge is one of the properties of an elementary particle, and its quantity takes a positive sign or negative sign corresponding to the electron or the hole, respectively. The spin angular momentum is the angular momentum of elementary particles such as electrons and quarks, and complex particles possess one of the quantum degeneracies. On the other hand, the wave function is called orbital as a quantum dynamical concept corresponding to an orbit for classical electrons. Both the spin and the orbital angular momentum are ascribed to the total angular momentum of particles.

The Schrödinger equation is written as

$$\mathcal{H}\psi(\mathbf{r}) = E\psi(\mathbf{r}), \tag{1.9}$$

using the Hamiltonian defined as

$$\mathcal{H} = -\frac{\hbar^2}{2m_e}\nabla^2 + V(r). \tag{1.10}$$

Now, as long as the wave function is written as $\psi(\mathbf{r}) = f(r)Y(\theta, \varphi)$, the radial and angle wave equations are, respectively, given by

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}Y(\theta, \varphi) + \chi Y(\theta, \varphi) = 0 \tag{1.11}$$

and

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+\frac{2m}{\hbar^2}\left(E-V(r)-\frac{\chi}{r^2}\right)f(r)=0, \tag{1.12}$$

where χ $(=l(l+1))$ is a constant with no dimension. Furthermore, by using the relationship of $Y(\theta,\varphi)=\Theta(\theta)\Phi(\varphi)$, Eq. 1.11 is converted to

$$\frac{d^2\Phi}{d\varphi^2}+\nu\Phi=0 \tag{1.13}$$

and

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Phi}{d\theta}\right)+\left(\chi-\frac{\nu}{\sin^2\theta}\theta\right)=0. \tag{1.14}$$

The solution of Eq. 1.13 is

$$\Phi=\frac{1}{\sqrt{2\pi}}\exp(im\varphi), \tag{1.15}$$

where $\nu=m^2$.

On the other hand, Eq. 1.14 is rewritten as

$$\frac{d}{d\omega}\left(1-\omega^2\right)\frac{dP}{d\omega}+\left(\chi-\frac{m^2}{1-\omega^2}\right)P=0, \tag{1.16}$$

where $\omega=\cos\theta$. P is called the associated Legendre function and is specified as

$$P_l^m(\omega)=(1-\omega^2)^{1/2|m|}\frac{d^{|m|}}{d\omega^{|m|}}P_l(\omega). \tag{1.17}$$

Thus,

$$Y_{l,m}(\theta,\varphi)=C_{l,m}P_l^m(\cos\theta)\Phi(\varphi) \tag{1.18}$$

$$=C_{l,m}P_l^m(\cos\theta)\frac{1}{\sqrt{2\pi}}\exp(im\varphi), \tag{1.19}$$

where

$$C_{l,m}=(-1)^{(m+|m|)/2}\frac{1}{\sqrt{2\pi}}\left[\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2}. \tag{1.20}$$

The wave function is finally expressed as

$$\varphi_{l,m}=f(r)Y_l^m(\theta,\varphi). \tag{1.21}$$

Therefore, the wave function of $3d$ orbitals for $(l, m) = (2, 0)$ is calculated as

$$\varphi_{2,0}(\mathbf{r}) = (-1)^0 \frac{1}{\sqrt{2\pi}} \sqrt{\frac{5}{2}} f \frac{1}{2^2 2!} (1 - \cos\theta)^0 \frac{\mathrm{d}^2}{\mathrm{d}^2 \cos\theta} (\cos^2\theta - 1)^2 \tag{1.22}$$

$$= \sqrt{\frac{5}{16\pi}} f (3\cos\theta^2 - 1) \tag{1.23}$$

$$= \sqrt{\frac{5}{16\pi}} f \frac{1}{r^2} (3z^2 - r^2). \tag{1.24}$$

Please note here the relationship of $x = r\sin\theta\cos\varphi$, $y = r\sin\theta\sin\varphi$, and $z = r\cos\theta$. A similar procedure brings about

$$\varphi_{2,1\pm}(\mathbf{r}) = \sqrt{\frac{15}{4\pi}} f \frac{1}{r^2} zx, \sqrt{\frac{15}{4\pi}} f \frac{1}{r^2} yz \tag{1.25}$$

and

$$\varphi_{2,2\pm}(\mathbf{r}) = \sqrt{\frac{15}{16\pi}} f \frac{1}{r^2} (x^2 - y^2), \sqrt{\frac{15}{16\pi}} f \frac{1}{r^2} xy. \tag{1.26}$$

Among them, the relative probability fixed by the last wave function, where electrons distribute, is proportional to $(x^2y^2 =) \sin^4\theta\cos^2\varphi\sin^2\varphi$. As shown in Fig. 1.1a, $\sin^4\theta$ mainly has finite values around $\pi/2$ and $3/2\pi$, which means most electrons disperse on the x-y plane. What is more, the $\cos^2\varphi\sin^2\varphi$ curve in Fig. 1.1b suggests that electrons spread over toward a diagonal-line direction (see also $3d_{xy}$ in Fig. 1.2). Five orbitals $\varphi_{2,0}(r)$, $\varphi_{2,1\pm}(r)$, and $\varphi_{2,2\pm}(r)$ are degenerate, but they are known to split into lower levels (t_{2g}) and higher levels (e_g) in the case of the ideal MO_6 octahedron due to the crystal field splitting. This orbital splitting can be interpreted intuitively as follows: $3z^2$-r^2 and x^2-y^2 orbitals in the e_g level turn to the position of O^{2-} ions (see Fig. 1.2). Coulomb interaction becomes strong due to negative charges at a close range, resulting in the e_g orbitals relatively going up compared to the t_{2g} orbitals.

More quantitatively, in the case of trigonal symmetry, the whole electric field is

$$V(\mathbf{r}) = V_2^0 + V_4^0 + V_4^3 \tag{1.27}$$

$$= A_2^0(3z^2 - r^2) + A_4^0(35z^4 - 30z^2r^2 + 3r^4) + A_4^3(x^3 - 3xy^2)z \tag{1.28}$$

and each component is written as

$$\sum(3z^2 - r^2) = \alpha < r^2 > [3L_z^2 - L(L+1)], \tag{1.29}$$

$$\sum(35z^4 - 30z^2r^2 + 3r^4) = \beta < r^4 > [35L_z^4 - 30L(L+1)L_z^2 + 25L_z^2 - 6L(L+1) + 3L^2(L+1)^2], \tag{1.30}$$

and

$$\sum(x^3 - 3xy^2)z = \frac{\beta}{4} < r^4 > [L_z(L_+^3 + L_-^3) + (L_+^3 + L_-^3)L_z]. \tag{1.31}$$

Hereafter, let's calculate the detailed energy level. First we estimate V_4^3, including the matrix element.

$$L_+^2 = \begin{pmatrix} 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{6} & 0 & 0 \\ 0 & 0 & 0 & \sqrt{6} & 0 \\ 0 & 0 & 0 & 0 & 2 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{6} & 0 & 0 \\ 0 & 0 & 0 & \sqrt{6} & 0 \\ 0 & 0 & 0 & 0 & 2 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 2\sqrt{6} & 0 & 0 \\ 0 & 0 & 0 & 6 & 0 \\ 0 & 0 & 0 & 0 & 2\sqrt{6} \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \tag{1.32}$$

$$L_+^3 = \begin{pmatrix} 0 & 0 & 0 & 12 & 0 \\ 0 & 0 & 0 & 0 & 12 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \tag{1.33}$$

A symmetric procedure on the matrix elements brings about

$$L_-^3 = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 12 & 0 & 0 & 0 & 0 \\ 0 & 12 & 0 & 0 & 0 \end{pmatrix}. \tag{1.34}$$

The first and second terms in Eq. 1.31, respectively, become

$$L_z(L_+^3 + L_-^3) = \begin{pmatrix} 2 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & -2 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 & 12 & 0 \\ 0 & 0 & 0 & 0 & 12 \\ 0 & 0 & 0 & 0 & 0 \\ 12 & 0 & 0 & 0 & 0 \\ 0 & 12 & 0 & 0 & 0 \end{pmatrix}$$

$$= \begin{pmatrix} 0 & 0 & 0 & 24 & 0 \\ 0 & 0 & 0 & 0 & 12 \\ 0 & 0 & 0 & 0 & 0 \\ -12 & 0 & 0 & 0 & 0 \\ 0 & -24 & 0 & 0 & 0 \end{pmatrix} \tag{1.35}$$

and

$$(L_+^3 + L_-^3)L_z = \begin{pmatrix} 0 & 0 & 0 & -12 & 0 \\ 0 & 0 & 0 & 0 & -24 \\ 0 & 0 & 0 & 0 & 0 \\ 24 & 0 & 0 & 0 & 0 \\ 0 & 12 & 0 & 0 & 0 \end{pmatrix}. \tag{1.36}$$

Thus,

$$L_z(L_+^3 + L_-^3) + (L_+^3 + L_-^3)L_z = \begin{pmatrix} 0 & 0 & 0 & 12 & 0 \\ 0 & 0 & 0 & 0 & -12 \\ 0 & 0 & 0 & 0 & 0 \\ 12 & 0 & 0 & 0 & 0 \\ 0 & -12 & 0 & 0 & 0 \end{pmatrix}. \tag{1.37}$$

For easy calculation of the eigenvalue, the matrix elements are rearranged in order of $M = 0, 1, -2, -1$, and 2 instead of the present alignment of $M = 2, 1, 0, -1$, and -2.

$$L_z(L_+^3 + L_-^3) + (L_+^3 + L_-^3)L_z = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -12 & 0 & 0 \\ 0 & -12 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 12 \\ 0 & 0 & 0 & 12 & 0 \end{pmatrix}. \tag{1.38}$$

Here we replace $-3A_2^0\alpha < r^2 >= A$, $12A_4^0\beta < r^4 >= B$, and $-3A_4^3\beta < r^4 >= C$. The two residual electric fields are expressed as follows:

$$V_2^0 = \alpha < r^2 > A_2^0(3M^2 - 6) \tag{1.39}$$

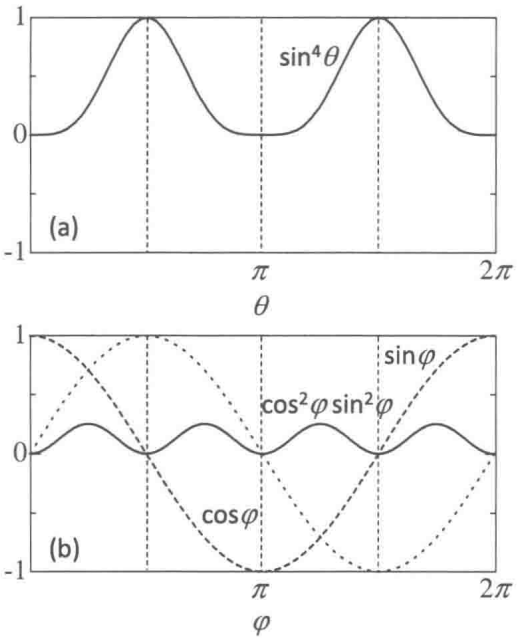

Figure 1.1 Functions of (a) $\sin^4\theta$ and (b) $\cos^2\varphi \sin^2\varphi$ together with $\sin\varphi$ (dotted curve) and $\cos\varphi$ (dashed curve).

and

$$V_4^0 = \beta < r^4 > A_4^0(35M^4 - 155M^2 + 72), \tag{1.40}$$

and thereby

$$V_2^0 = \begin{cases} 2A & (M = 0) \\ A & (M = 1) \\ -2A & (M = -2) \\ A & (M = -1) \\ -2A & (M = 2) \end{cases} \tag{1.41}$$

and

$$V_4^0 = \begin{cases} 6B & (M = 0) \\ -4B & (M = 1) \\ B & (M = -2) \\ -4B & (M = -1) \\ B & (M = 2). \end{cases} \tag{1.42}$$