CHAPTER 28
SPECTROSCOPIC MEASUREMENTS

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28.1 GLOSSARY

$A_{ba}$ Einstein coefficient for spontaneous emission
$a_o$ Bohr radius
$B_{uf}$ Einstein coefficient between initial state $|i\rangle$ and final state $|f\rangle$
$e$ charge on the electron
ED electric dipole term
$E_{DC}$ Dirac Coulomb term
$E_{hf}$ hyperfine energy
$E_n$ eigenvalues of quantum state $n$
EQ electric quadrupole term
$E(t)$ electric field at time $t$
$E(\omega)$ electric field at frequency $\omega$
$g_o$ degeneracy of ground level
$g_e$ degeneracy of excited level
$g_N$ gyromagnetic ratio of nucleus
$h$ Planck's constant
$H_{SO}$ spin-orbit interaction hamiltonian
$I$ nuclear spin
$I(t)$ the emission intensity at time $t$
$j$ total angular momentum vector given by $j = 1 \pm \frac{1}{2}$
$l_o$ orbital state
$m$ mass of the electron
MD magnetic dipole term
$M_N$ mass of nucleus $N$
28.2 OPTICAL MEASUREMENTS

\[ n_e(T) \quad \text{equilibrium number of photons in a blackbody cavity radiator at angular frequency } \omega \text{ and temperature } T \]

QED quantum electrodynamics

\[ R_n(r) \quad \text{radial wavefunction} \]

\[ R_n \quad \text{Rydberg constant for an infinitely heavy nucleus} \]

\[ s \quad \text{spin quantum number with the value } \frac{1}{2} \]

\[ s_i \quad \text{electronic spin} \]

\[ T \quad \text{absolute temperature} \]

\[ W_{ab} \quad \text{transition rate in absorption transition between states } a \text{ and } b \]

\[ W_{ba} \quad \text{transition rate in emission transition from state } b \text{ to state } a \]

\[ Z \quad \text{charge on the nucleus} \]

\[ \alpha = e^2/4\pi\varepsilon_0hc \quad \text{fine structure constant} \]

\[ \Delta \omega \quad \text{natural linewidth of the transition} \]

\[ \Delta \omega_D \quad \text{Doppler width of transition} \]

\[ \varepsilon_0 \quad \text{permittivity of free space} \]

\[ \xi(r) \quad \text{spin-orbit parameter} \]

\[ \mu_B \quad \text{Bohr magneton} \]

\[ \rho(\omega) \quad \text{energy density at frequency } \omega \]

\[ \tau_R \quad \text{radiative lifetime} \]

\[ \omega \quad \text{angular velocity} \]

\[ \omega_k \quad \text{mode } k \text{ with angular frequency } \omega \]

\[ (f|v'|i) \quad \text{matrix element of perturbation } V \]

28.2 INTRODUCTORY COMMENTS

The conceptual basis of optical spectroscopy and its relationship to the electronic structure of matter as presented in the article entitled “Optical Spectroscopy and Spectroscopic Lineshapes” in Vol. I, Chap. 8 of this Handbook. The article entitled “Optical Spectrometers” in Vol. II, Chap. 20 of this Handbook discusses the operating principles of optical spectrometers. This article illustrates the underlying themes of the earlier ones using the optical spectra of atoms, molecules, and solids as examples.

28.3 OPTICAL ABSORPTION MEASUREMENTS OF ENERGY LEVELS

Atomic Energy Levels

The interest in spectroscopic measurements of the energy levels of atoms is associated with tests of quantum theory. Generally, the optical absorption and luminescence spectra of atoms reveal large numbers of sharp lines corresponding to transitions between the stationary states. The hydrogen atom has played a central role in atomic physics because of the accuracy with which relativistic and quantum electrodynamic shifts to the one-electron energies can be calculated and measured. Tests of quantum electrodynamics usually
Spectroscopy is shown to advantage in measurements of the $^2S$ tritium. Techniques give a wave function and energy eigenvalue which are exact, for all practical levels are $^1S$, $^2S$, $^2P$, and $^2P$ in order of increasing energy. The $^1S$ splitting is of order 20.60 eV and transitions between these levels are not excited by optical photons. Transitions involving the $^2S$ and $^2P$ levels, respectively, and higher-lying spin singlet and spin triplet states occur at optical wavelengths. Experimental work on atomic helium has emphasized the lower-lying triplet levels, which have long excited-state lifetimes and large quantum electrodynamic (QED) shifts.

As with hydrogen, the spectra of He atoms are inhomogeneously broadened by the Doppler effect. Precision measurements have been made using two-photon laser spectroscopy (e.g., $2S\rightarrow nS$ $(n = 4–6)$ and $nD$ $(n = 3–6)$, or laser saturation absorption spectroscopy ($2S\rightarrow 2P$ and $3P\rightarrow 3D$). The $2S\rightarrow 3P$ and two-photon $2S\rightarrow nD$ $(n = 3–7)$ spectra have been measured using dye lasers. The wide tune ranging of the Ti-sapphire laser and the capability for generating frequencies not easily accessible with dye lasers using frequency-generation techniques makes it an ideal laser to probe transitions starting on the $2S$ levels of He. Two examples are the two-photon transition $2S\rightarrow 3S$ at 855 nm and the $2S\rightarrow 3P$ transition at 389 nm. The power of Doppler-free spectroscopy is shown to advantage in measurements of the $2S\rightarrow 2P$ transition. Since both $S$ and $P$ are excited levels, the homogeneous width is determined by the sum of the reciprocal lifetimes of the two levels. Since both $2S$ and $2P$ levels are long-lived, the resulting homogeneous width is comparatively narrow. Figure 1a shows the Doppler-broadened profile of the $2S\rightarrow 2P$ transition of $^4$He for which the FWHM is about 5.5 GHz. The inhomogeneously broadened line profile shown in Fig. 1a also shows three very weak “holes” corresponding to saturated absorption of the Ti-sapphire laser radiation used to carry out the experiment. These components correspond to the $2S\rightarrow 3P$, and $2S\rightarrow 3P$, transitions and their crossover resonance. The amplitude of the saturated signal is some 1–2 percent of the total absorption. The relativistic splittings including spin-orbit coupling of $P\rightarrow P$ and $P\rightarrow P$ are 8.1 GHz and 658.8 MHz, respectively. Frequency modulation of the laser (see Vol. 2, Chap. 20 of this Handbook) causes the “hole” to be detected as a first derivative of the absorption line, Fig. 1b. The observed FWHM of the Doppler-free signals was only 20 MHz. The uncertainty in the measured $2S\rightarrow 3P$ interval was two parts in $10^8$ (i.e., 1.5 MHz), an improvement by a factor of sixty on earlier measurements. A comparison of the experimental results with recent calculations of the non-QED terms gives a value for the one-electron Lamb shift of $-346.5$ (2.8) MHz, where the uncertainty in the quoted magnitude is in parentheses. The theoretical value is $-346.3$ (13.9) MHz. Finally, the frequencies of the $2S\rightarrow 3P$, $3P$ transitions were determined to be $25708.60959$ (5) cm$^{-1}$ and $25708.58763$ (5) cm$^{-1}$, respectively.

The $^1$He ion is another two-electron system, of some importance in astrophysics. It is the simplest quantum mechanical three-body species. Approximate quantum mechanical techniques give a wave function and energy eigenvalue which are exact, for all practical purposes. Experimentally, the optical absorption spectrum of $^1$He is continuous, a property of importance in understanding the opacity of the sun. $^1$He does not emit radiation in characteristic emission lines. Instead the system sheds its excess (absorbed) energy by
ejecting one of the electrons. The radiant energy associated with the ejected electron consists of photons having a continuous energy distribution. Recent measurements with high-intensity pulsed lasers, counterpropagating through beams of 800-MeV H\(^-\) ions, have produced spectacular “doubly excited states” of the He\(^-\) ion. Such ions are traveling at 84 percent of the velocity of light and, in this situation, the visible laboratory photons are shifted into the vacuum ultraviolet region. At certain energies the H\(^-\) ion is briefly excited into a system in which both electrons are excited prior to one of the electrons being ejected. Families of new resonances up to the energy level \(N = 8\) have been observed.\(^{12}\) These resonances are observed as windows in the continuous absorption spectrum, at energies given by a remarkably simple relation reminiscent of the Bohr equation for the Balmer series in hydrogen.\(^{13}\) The resonance line with the lowest energy in each family corresponds to both electrons at comparable distances from the proton.

These experiments on H\(^-\) are but one facet of the increasingly sophisticated measurements designed to probe the interaction between radiation and matter driven by
experiments in laser technology. “Quantum jump” experiments involving single ions in an
electromagnetic trap have become almost commonplace. Chaos has also become a rapidly
growing subfield of atomic spectroscopy. The particular conditions under which chaos
may be observed in atomic physics include hydrogenic atoms in strong homogeneous
magnetic fields such that the cyclotron radius of the electron approaches the dimensions of
the atomic orbitals. A more easily realizable situation using magnetic field strengths of
only a few tesla uses highly excited orbitals close to the ionization threshold. Iu et al. have
reported the absorption spectrum of transitions from the 3s state of Li to bound and
continuum states near the ionization limit in a magnetic field of ca. six tesla. There is a
remarkable coincidence between calculations involving thousands of energy levels and
experiments involving high-resolution laser spectroscopy.

Atomic processes play an important role in the energy balance of plasmas, whether they
be created in the laboratory or in star systems. The analysis of atomic emission lines gives
much information on the physical conditions operating in a plasma. In laser-produced
plasmas, the densities of charged ions may be in the range $10^{20}$–$10^{25}$ ions $cm^{-3}$, depending
on the pulse duration of the laser. The spectra of many-electron ions are complex and may
have the appearance of an unresolved transition array between states belonging to specific
initial and final configurations. Theoretical techniques have been developed to determine
the average ionization state of the plasma from the observed optical spectrum. In many
cases, the spectra are derived from ionic charge states in the nickel-like configuration
containing 28 bound electrons. In normal nickel, the outer shell configuration is $(3d^8)(4s^2)$,
the 4s levels having filled before 3d because the electron–electron potentials are stronger
than electron-nuclear potentials. However, in highly ionized systems, the additional
electron-nuclear potential is sufficient to shift the configuration from $(3d^8)(4s^2)$ to the
closed shell configuration $(3d^{10})$. The resulting spectrum is then much simpler than for
atomic nickel. The Ni-like configuration has particular relevance in experiments to make
x-ray lasers. For example, an analog series of collisionally pumped lasers using Ni-like ions
has been developed, including a Ta$^{45+}$ laser operating at 4.48 nm and a W$^{46+}$ laser
operating at 4.32 nm.

Molecular Spectroscopy

The basic principles of gas-phase molecular spectroscopy were also discussed in “Optical
Spectroscopy and Spectroscopic Lineshapes”, Vol. I, Chap. 8 of this Handbook. The
spectra of even the simplest molecules are complicated by the effects of vibrations and of
rotations about an axis. This complexity is illustrated elsewhere in this Handbook in Fig. 8
of Vol. I, Chap. 8, “Optical Spectroscopy and Spectroscopic Lineshapes,” which depicts a
photographically recorded spectrum of the $2\Pi \rightarrow 2\Sigma$ bands of the diatomic molecule NO,
which was interpreted in terms of progressions and line sequences associated with the $P$–
$Q$– and $R$-branches. The advent of Fourier transform spectroscopy has led to great
improvements in resolution and greater efficiency in revealing all the fine details that
characterize molecular spectra. Figure 2a is a Fourier-transform infrared spectrum of
nitrous oxide, $N_2O$, which shows the band center at 2462 cm$^{-1}$ flanked by the $R$-branch
and a portion of the $P$-branch; the density of lines in the $P$- and $R$-branch is evident. On
an expanded scale, in Fig. 2b, there is a considerable simplification of the rotational-
 vibrational structure at the high-energy portion of the $P$-branch. The weaker lines are the
so-called “hot bands.”

More precise determinations of the transition frequencies in molecular physics are
measured using Lamb dip spectroscopy. The spectrum shown in Fig. 3a is a portion of the
laser Stark spectrum of methyl fluoride measured using electric fields in the range
20–25 kV cm$^{-1}$ with the 9-$\mu$m $P(18)$ line of the CO$_2$ laser, which is close to the $v_1$
band origin of CH$_3$F. The spectrum in Fig. 3a consists of a set of $\Delta M_l = \pm 1$ transitions, brought
into resonance at different values of the static electric field. Results from the alternative
high-resolution technique using a supersonic molecular beam and bolometric detector are shown in Fig. 3b: this spectrum was obtained using CH$_3$F in He mixture expanded through a 35-μm nozzle. The different $M_J$ components of the $Q(1,0)$, $Q(2,1)$, and $Q(3,3)$ components of the $Q$-branch are shown to have very different intensities relative to those in Fig. 3a on account of the lower measurement temperature.

There is considerable interest in the interaction of intense laser beams with molecules. For example, when a diatomic molecule such as N$_2$ or CO is excited by an intense ($10^{15}$ W cm$^{-2}$), ultrashort (0.6 ps) laser pulse, it multiply ionizes and then fragments as a
FIGURE 3  (a) Laser Stark absorption spectrum of methyl fluoride measured at 300 K using Lamb dip spectroscopy with a gas pressure of 5 m Torr; (b) the improved resolution obtained using molecular-beam techniques with low-temperature bolometric detection and CHF in He expanded through a 35-μm nozzle. (After C. Douketic and T. E. Gough).17

consequence of Coulomb repulsion. The charge and kinetic energy of the resultant ions can be determined by time-of-flight (TOF) mass spectrometry. In this technique, the daughter ions of the “Coulomb explosion” drift to a cathode tube at different times, depending on their weight. In traditional methods, the TOF spectrum is usually averaged over many laser pulses to improve the signal-to-noise ratio. Such simple averaging procedures remove the possibility of correlations between particular charged fragments. This problem has been overcome by the covariance mapping technique developed by Frasinski and Codling.18 Experimentally, a linearly polarized laser pulse with E-vector pointing towards the detector is used to excite the molecules, which line up with their
internuclear axis parallel to the E-field. Under Coulomb explosion, one fragment heads toward the detector and the other away from the detector. The application of a dc electric field directs the “backward” fragment ion to the detector, arriving at some short time after the forward fragment. This temporal separation of two fragments arriving at the detector permits the correlation between molecular fragments to be retained. In essence, the TOF spectrum, which plots molecular weight versus counts, is arranged both horizontally (forward ions) and vertically (backward ions) on a two-dimensional graph. A coordinate point on a preliminary graph consists of two ions along with their counts during a single pulse. Coordinates from $10^5$ pulses or so are then assembled in a final map. Each feature on the final map relates to a specific fragmentation channel, i.e., the pair of fragments and their parent molecule. The strength of the method is that it gives the probability for the creation and fragmentation of the particular parent ion. Covariance mapping experiments on $N_2$ show that 610-nm and 305-nm pulses result in fragmentation processes that are predominantly charge-symmetric. In other words, the Coulomb explosion proceeds via the production of ions with the same charge.

Optical Spectroscopy of Solids

One of the more fascinating aspects of the spectroscopy of electronic centers in condensed matter is the variety of lineshapes displayed by the many different systems. Those already discussed in this Handbook include $\text{Nd}^{3+}$ in YAG (Vol. I, Chap. 8, Fig. 6), $\text{O}_2^-$ in KBr (Vol. I, Chap. 8, Fig. 11), $\text{Cr}^{3+}$ in YAG (Vol. I, Chap. 8, Fig. 12), and $\text{F}$ centers in KBr (Vol. I, Chap. 8, Fig. 13). The very sharp $\text{Nd}^{3+}$ lines (in Vol. I, Chap. 8, Fig. 6) are zero-phonon lines, inhomogeneously broadened by strain. The abundance of sharp lines (in Vol. I, Chap. 8) is characteristic of the spectra of trivalent rare-earth ions in ionic crystals. Typical low-temperature linewidths for $\text{Nd}^{3+}$: YAG are 0.1–0.2 cm$^{-1}$. There is particular interest in the spectroscopy of $\text{Nd}^{3+}$ because of the efficient laser transitions from the $^4F_{9/2}$ level into the $^4I_{15/2}$-manifold. The low-temperature luminescence transitions between $^4F_{9/2} \rightarrow ^4I_{15/2}, ^4I_{13/2}, ^4I_{11/2}$ and $^4I_{9/2}$ levels are shown in Fig. 6 (“Optical Spectroscopy and Spectroscopic Lineshapes”): all are split by the effects of the crystalline electric field. Given the relative sharpness of these lines, it is evident that the Slater integrals $F^{(k)}$, spin-orbit coupling parameters $\zeta$, and crystal field parameters, $B_k^t$, may be measured with considerable accuracy. The measured values of the $F^{(k)}$ and $\zeta$ vary little from one crystal to another.\textsuperscript{19} However, the crystal field parameters, $B_k^t$, depend strongly on the rare-earth ion-ligand ion separation. Most of the 4f ions have transitions which are the basis of solid-state lasers. Others such as $\text{Eu}^{3+}$ and $\text{Tb}^{3+}$ are important red-emitting and green-emitting phosphor ions, respectively.\textsuperscript{20}

Transition-metal ion spectra are quite different from those of the rare-earth ions. In both cases, the energy-level structure may be determined by solving the Hamiltonian

\begin{equation}
H = H_o + H' + H_{so} + H_c
\end{equation}

in which $H_o$ is a sum of one-electron Hamiltonians including the central field of each ion, $H'$ is the interaction between electrons in the partially-filled 3d or 4f orbitals, $H_{so}$ is the spin-orbit interaction, and $H_c$ is the interaction of the outer shell electrons with the crystal field. For rare-earth ions $H'$, $H_{so} \gg H_c$, and the observed spectra very much reflect the free-ion electronic structure with small crystal field perturbations. The spectroscopy of the transition-metal ions is determined by the relative magnitudes of $H' = H_c$.\textsuperscript{19,21} The simplest of the transition-metal ions is $\text{Ti}^{3+}$: in this 3d$^2$ configuration a single 3d electron resides outside the closed shells. In this situation, $H' = 0$ and only the effect of $H_c$ needs be considered (Fig. 4a). The $\text{Ti}^{3+}$ ion tends to form octahedral complexes, where the 3d configuration is split into $^2E$ and $^2T_2$ states with energy separation $10D_{q}$. In cation sites with weak, trigonally symmetric distortions, as in $\text{Al}_2\text{O}_3$ and $\text{Y}_2\text{Al}_2\text{O}_{12}$, the lowest-lying
state, \( ^2T_2 \), splits into \( ^2A_1 \) and \( ^2E \) states (using the \( C_n \) group symmetry labels). In oxides, the octahedral splitting is of order \( 10D_q = 20,000 \text{ cm}^{-1} \) and the trigonal field splitting \( \nu = 700 - 1000 \text{ cm}^{-1} \). Further splittings of the levels occur because of spin-orbit coupling and the Jahn-Teller effect. The excited \( ^2E \) state splits into \( ^2A \) and \( ^2E \) (from \( ^2A_1 \)), and \( ^2E \) and \( ^2A \) (from \( ^2E \)). The excited state splitting by a static Jahn-Teller effect is large, \( \sim 2000 - 2500 \text{ cm}^{-1} \), and may be measured from the optical absorption spectrum. In contrast, ground-state splittings are quite small: a dynamic Jahn-Teller effect has been shown to strongly quench the spin-orbit coupling \( \zeta \) and trigonal field splitting \( \nu \) parameters. In \( \text{Ti}^{3+}:\text{Al}_2\text{O}_3 \) the optical absorption transition, \( ^2T_2 \rightarrow ^2E \), measured at 300 K, Fig. 4b, consists of two broad overlapping bands separated by the Jahn-Teller splitting, the composite band having a peak at ca. 20,000 cm\(^{-1} \). Luminescence occurs only from the lower-lying excited state \( ^2A \), the emission band peak occurring at ca. 14,000 cm\(^{-1} \). As Fig. 4 shows, both absorption and emission bands are broad because of strong electron-phonon coupling. At low temperatures the spectra are characterized by weak zero-phonon lines, one in absorption due to transitions from the \( ^2A \) ground state and three in emission corresponding to transitions in the \( E \), \( E \), and \( ^2A \) levels of the electronic ground state. These transitions are strongly polarized.

For ions with 3d\(^n\) configuration it is usual to neglect \( H_c \) and \( H_o \) in Eq. (1), taking into account only the central ion terms and the Coulomb interaction between the 3d electrons. The resulting energies of the free-ion LS terms are expressed in terms of the Racah parameters \( A \), \( B \), and \( C \). Because energy differences between states are measured in spectroscopy, only \( B \) and \( C \) are needed to categorize the free-ion levels. For pure d-functions, \( C/B = 4.0 \). The crystal field term \( H_c \) and \( H_o \) also are treated as perturbations. In many crystals, the transition-metal ions occupy octahedral or near-octahedral cation
The splittings of each free-ion level by an octahedral crystal field depend in a complex manner on $B$, $C$, and the crystal field strength $D_q$ given by

$$D_q = \frac{Ze^2}{24\pi\varepsilon_0} \left( \frac{r^*}{a^*} \right)^3 \tag{2}$$

The parameters $D$ and $q$ always occur as a product. The energy levels of the 3d$^n$ transition-metal ions are usually represented on Tanabe-Sugano diagrams, which plot the energies $E(I)$ of the electronic states as a function of the octahedral crystal field. The crystal field levels are classified by irreducible representations $I'$ of the octahedral group, $O_h$. The Tanabe-Sugano diagram for the 3d$^n$ configuration, shown in Fig. 5a, was constructed using a $C/B$ ratio = 4.8: the vertical broken line drawn at $D_q/B = 2.8$ is appropriate for Cr$^{3+}$ ions in ruby. If a particular value of $C/B$ is assumed, only two variables, $B$ and $D_q$, need to be considered: in the diagram $E(I)/B$ is plotted as a function of $D_q/B$. The case of ruby, where the $^2E$ level is below $^4T_2$, is referred to as the strong field case. Other materials where this situation exists include YAlO$_3$, Y$_3$Al$_5$O$_{12}$ (YAG), and MgO. In many fluorides, Cr$^{3+}$ ions occupy weak field sites, where $E(^4T_2) < E(^2E)$ and $D_q/B$ is less than 2.2. When the value of $D_q/B$ is close to 2.3, the intermediate crystal field, the $^4T_2$ and $^2E$ states almost degenerate. The value of $D_q/B$ at the level crossing between $^4T_2$ and $^2E$ depends slightly on the value of $C$.

The Tanabe-Sugano diagram represents the static lattice. In practice, electron-phonon coupling must be taken into account: the relative strengths of coupling to the states involved in transitions and the consequences may be inferred from Fig. 5a. Essentially, ionic vibrations modulate the crystal field experienced by the central ion at the vibrational frequency. Large differences in slope of the $E$ versus $D_q$ graphs indicate large differences.

**FIGURE 5** The Tanabe-Sugano diagram for Cr$^{3+}$ ions with $C/B = 4.8$, appropriate for ruby for which $D_q/B = 2.8$. On the right of the figure are shown the optical absorption and photoluminescence spectrum of ruby measured at 300 K.
in coupling strengths and hence large homogeneous bandwidths. Hence, absorption and luminescence transitions from the \( ^3\!A_2 \) ground state to the \( ^4\!T_2 \) and \( ^4\!T_1 \) states will be broadband due to the large differences in coupling of the electronic energy to the vibrational energy. For the \( ^4\!A_2 \rightarrow ^4\!E, ^4\!T_1 \) transition, the homogeneous linewidth is hardly affected by lattice vibrations, and sharp line spectra are observed.

The \( \text{Cr}^{3+} \) ion occupies a central position in the folklore of transition-metal ion spectroscopy, having been studied by spectroscopists for over 150 years. An extensive survey of \( \text{Cr}^{3+} \) luminescence in many compounds was published as early as 1932.\(^{24}\) The \( \text{Cr}^{3+} \) ions have the outer shell configuration, \( 3d^3 \), and their absorption and luminescence spectra may be interpreted using Fig. 5. First, the effect of the octahedral crystal field is to remove the degeneracies of the free-ion states \( ^4\!F \) and \( ^4\!G \). The ground term of the free ion, \( ^4\!F_{2g} \), is split by the crystal field into a ground-state orbital singlet, \( ^4\!A_{2g} \), and two orbital triplets \( ^4\!T_{2g} \) and \( ^4\!T_{1g} \) in order of increasing energy. Using the energy of the \( ^4\!A_2 \) ground state as the zero, for all values of \( D_q/B \), the energies of the \( ^4\!T_{2g} \) and \( ^4\!T_{1g} \) states are seen to vary strongly as a function of the octahedral crystal field. In a similar vein, the \( ^4\!G \) free-ion state splits into \( ^4\!E, ^4\!T_2, ^4\!T_1, \) and \( ^4\!A_1 \) states, the two lowest of which, \( ^4\!E \) and \( ^4\!T_1 \), vary very little with \( D_q \). The energies \( E(\!^4\!T_2) \) and \( E(\!^4\!A_1) \) are also only weakly dependent on \( D_q/B \).

The free-ion term, \( ^4\!P \), which transforms as the irreducible representation \( ^4\!T_1 \) of the octahedral group is derived from \( (e^2t^6) \) configuration: this term is not split by the octahedral field although its energy is a rapidly increasing function of \( D_q/B \). Low-symmetry distortions lead to strongly polarized absorption and emission spectra.\(^{25}\)

The \( \sigma \)-polarized optical absorption and luminescence spectra of ruby are shown in Fig. 5b. The expected energy levels predicted from the Tanabe-Sugano diagram are seen to coincide with appropriate features in the absorption spectrum. The most intense features are the vibronically broadened \( ^4\!A_2 \rightarrow ^4\!T_2, ^4\!T_1 \) transitions. These transitions are broad and characterized by large values of the Huang-Rhys factor \((S = 6–7) \). These absorptions occur in the blue and yellow-green regions, thereby accounting for the deep red color of ruby. Many other \( \text{Cr}^{3+} \)-doped hosts have these bands in the blue and orange-red regions, by virtue of smaller values of \( D_q/B \); the colors of such materials (e.g., \( \text{MgO}, \text{Gd}_2\text{Sc}_2\text{Ga}_3\text{O}_{12} \), \( \text{LiSrAlF}_6 \), etc.) are different shades of green. The absorption transitions, \( ^4\!A_2 \rightarrow ^4\!E, ^4\!T_2, ^4\!T_1 \) levels are spin-forbidden and weakly coupled to the phonon spectrum \((S < 0.5) \). The spectra from these transitions are dominated by sharp zero-phonon lines. However, the low-temperature photoluminescence spectrum of ruby is in marked contrast to the optical absorption spectrum since only the sharp zero-phonon line \((R\text{-line}) \) due to the \( ^4\!E \rightarrow ^4\!A_2 \) transition being observed. Given the small energy separations between adjacent states of \( \text{Cr}^{3+} \), the higher excited levels decay nonradiatively to the lowest level, \( ^4\!E \), from which photoluminescence occurs across a band gap of ca. 15,000 \( \text{cm}^{-1} \). Accurate values of the parameters \( D_q, B \), and \( C \) may be determined from these absorption data. First, the peak energy of the \( ^4\!A_2 \rightarrow ^4\!T_2 \) absorption band is equal to \( 10D_q \). The energy shift between the \( ^4\!A_2 \rightarrow ^4\!T_2, ^4\!T_1 \) bands is dependent on both \( D_q \) and \( B \), and the energy separation between the two broad absorption bands is used to determine \( B \). Finally, the position of the \( R \)-line varies with \( D_q, B \), and \( C \); in consequence, once \( D_q \) and \( B \) are known, the magnitude of \( C \) may be determined from the position of the \( ^4\!A_2 \rightarrow ^4\!E \) zero-phonon line.

This discussion of the spectroscopy of the \( \text{Cr}^{3+} \) ion is easily extended to other multielectron configurations. The starting points are the Tanabe-Sugano diagrams collected in various texts.\(^{19,21}\) Analogous series of elements occur in the fifth and sixth periods of the periodic table, respectively, where the 4d\(^{1} \) (palladium) and 5d\(^{1} \) (platinum) groups are being filled. Compared with electrons in the 3d shell, the 4d and 5d shell electrons are less tightly bound to the parent ion. In consequence, charge transfer transitions, in which an electron is transferred from the cation to the ligand ion (or vice versa), occur quite readily. The charge transfer transitions arise from the movement of electronic charge over a typical interatomic distance, thereby producing a large dipole moment and a concomitant large oscillator strength for the absorption process. For the Fe-group ions \((3d\text{ configuration})\), such charge transfer effects result in the absorption of ultraviolet photons.
For example the Fe$^{3+}$ ion in MgO absorbs in a broad structureless band with peak at 220 nm and half-width of order 120 nm (i.e., 0.3 eV). The Cr$^{2+}$ ion also absorbs by charge transfer process in this region. In contrast, the palladium and platinum groups have lower-lying charge transfer states. The resulting intense absorption bands in the visible spectrum may overlap spectra due to low-lying crystal field transitions. Rare-earth ions also give rise to intense charge transfer bands in the ultraviolet region.

Various metal cations have been used as broadband visible region phosphors. For example, transitions between the 4f$^n$ and 4f$^{n-1}$5d levels of divalent rare-earth ions give rise to intense broad transitions which overlap many of the sharp 4f$^n$ transitions of the trivalent rare-earth ions. Of particular interest are Sm$^{2+}$, Dy$^{2+}$, Eu$^{2+}$, and Tm$^{2+}$. In Sm$^{2+}$ (4f$^1$) broadband absorption transitions from the ground state $^7F_1$ to the 4f$^0$ 5d level may result in either broadband emission (from the vibronically relaxed 4f$^0$ 5d level) or sharp line emission from $^7D_0$ (4f$^1$) depending upon the host crystal. The 4f$^0$ 5d level, being strongly coupled to the lattice, accounts for this variability. There is a similar material-by-material variation in the absorption and emission properties of the Eu$^{2+}$ (4f$^1$ configuration), which has the $^5D_{0,2}$ ground level. The next highest levels are derived from the 4f$^0$ 5d state, which is also strongly coupled to the lattice. This state is responsible for the varying emission colors of Eu$^{2+}$ in different crystals, e.g., violet in Sr$_2$P$_2$O$_7$, blue in BaAl$_2$O$_3$, green in SrAl$_2$O$_4$, and yellow in Ba$_2$SiO$_5$.

The heavy metal ions Tl$^{+}$, In$^{+}$, Ga$^{3+}$, Sn$^{3+}$, and Pb$^{2+}$ may be used as visible-region phosphors. These ions all have two electrons in the ground configuration ns$^2$ and excited configurations (ns)$(np)$. The lowest-lying excited states, in the limit of Russell Saunders coupling, are then $^1S_0(ns)^2$, $^3P_{0,1,2}$, and $^1P_1$ from (ns)$(np)$. The spectroscopy of Tl$^+$ has been much studied especially in the alkali halides. Obviously $^1S_0\rightarrow^1P_1$ is the strongest absorption transition, occurring in the ultraviolet region. This is labeled as the C-band in Fig. 6. Next in order of observable intensity is the A-band, which is a spin-forbidden absorption.
SPECTROSCOPIC MEASUREMENTS

absorption transition $^1S_0 \rightarrow ^3P_1$, in which the relatively large oscillator strength is borrowed from the $^1P_1$ state by virtue of the strong spin-orbit interaction in these heavy metal ions. The $B$ and $D$ bands, respectively, are due to absorption transitions from $^1S_0$ to the $^3P_1$ and $^3P_0$ states induced by vibronic mixing. A phenomenological theory has been developed which quantitatively accounts for both absorption spectra and the triplet state emission spectra.

The examples discussed so far have all concerned the spectra of ions localized in levels associated with the central fields of the nucleus and closed-shells of electrons. There are other situations which warrant serious attention. These include electron-excess centers in which the positive potential of an anion vacancy in an ionic crystal will trap one or more electrons. The simplest theory treats such a color center as a particle in a finite potential well. The simplest such center is the $F$-center in the alkali halides, which consist of one electron trapped in an anion vacancy. As we have already seen (e.g., Fig. 13 in “Optical Spectroscopy and Spectroscopic Lineshapes”, Vol. I, Chap. 8 of this Handbook), such centers give rise to broadbands in both absorption and emission, covering much of the visible and near-infrared regions for alkali halides. $F$-aggregate centers, consisting of multiple vacancies arranged in specific crystallographic relationships with respect to one another, have also been much studied. They may be positive, neutral, or negative in charge relative to the lattice depending upon the number of electrons trapped by the vacancy aggregate.

Multiquantum wells (MQWs) and strained-layer superlattices (SLSs) in semiconductors are yet another type of finite-well potential. In such structures, alternate layers of two different semiconductors are grown on top of each other so that the bandgap varies in one dimension with the periodicity of the epitaxial layers. A modified Kronig-Penney model is often used to determine the energy eigenvalues of electrons and holes in the conduction and valence bands, respectively, of the narrower gap material. Allowed optical transitions between valence band and conduction band are then subject to the selection rule $\Delta n = 0$, where $n = 0, 1, 2, \ldots, \infty$. The example given in Fig. 7 is for SLSs in the II-VI family of semiconductors ZnS/ZnSe. The samples were grown by metalo-organic vapor phase epitaxy with a superlattice periodicity of ca. 6–8 nm while varying the thickness of the narrow gap material (ZnSe) between 0.8 nm and 7.6 nm. The splitting between the two

FIGURE 7 Optical absorption spectra of SLSs of ZnS/ZnSe measured at 14 K. (After Fang et al.)
sharp features occurs because the valence band states are split into “light holes” (lh) and “heavy holes” (hh) by spin-orbit interaction. The absorption transitions then correspond to transitions from the \( n = 1 \) lh- and hh-levels in the valence band to the \( n = 1 \) electron states in the conduction band. Higher-energy absorption transitions are also observed. After absorption, electrons rapidly relax down to the \( n = 1 \) level from which emission takes place down to the \( n = 1 \), lh-level in the valence band, giving rise to a single emission line at low temperature.

28.4 THE HOMOGENEOUS LINESHAPE OF SPECTRA

Atomic Spectra

The homogeneous widths of atomic spectra are determined by the uncertainty principle, and hence by the radiative decaytime, \( \tau_R \) (as discussed previously in this Handbook in Vol. I, Chap. 8, “Optical Spectroscopy and Spectroscopic Lineshapes”). Indeed, the so-called natural or homogeneous width of the transition, \( \Delta \omega \), is given by the Einstein coefficient for spontaneous emission, \( A_{\text{iso}} = (\tau_R)^{-1} \). The homogeneously broadened line has a Lorentzian lineshape with FWHM given by \( (\tau_R)^{-1} \). In gas-phase spectroscopy, atomic spectra are also broadened by the Doppler effect: random motion of atoms broadens the lines inhomogeneously leading to a Gaussian-shaped line with FWHM proportional to \( (T/M)^{1/2} \), where \( T \) is the absolute temperature and \( M \) the atomic mass. Saturated laser absorption or optical hole-burning (OHB) techniques are among the methods which recover the true homogeneous width of an optical transition. Experimental aspects of these types of measurement were discussed in this Handbook in Vol. II, Chap. 20, “Optical Spectroscopy”, and examples of Doppler-free spectra (Figs. 1 and 3, Vol. I, Chap. 8, “Optical Spectroscopy and Spectroscopic Lineshapes”) were discussed in terms of the fundamental tests of the quantum and relativistic structure of the energy levels of atomic hydrogen. Similar measurements were also discussed for the case of He (Fig. 1) and in molecular spectroscopy (Fig. 3). In such examples, the observed lineshape is very close to a true Lorentzian, typical of a lifetime-broadened optical transition.

Zero-phonon Lines in Solids

Optical hole-burning (OHB) reduces the effects of inhomogeneous broadening in solid-state spectra. For rare-earth ions, the homogeneous width amounts to some 0.1–1.0 MHz, the inhomogeneous widths being determined mainly by strain in the crystal. Similarly, improved resolution is afforded by fluorescence line narrowing (FLN) in the \( R \)-line of \( \text{Cr}^{3+} \) (Vol. I, Chap. 8, Fig. 12). However, although the half-width measured using OHB is the true homogeneous width, the observed FLN half-width, at least in resonant FLN, is a convolution of the laser width and twice the homogeneous width of the transition.\(^3\)\(^3\) In solid-state spectroscopy, the underlying philosophy of OHB and FLN experiments may be somewhat different from that in atomic and molecular physics. In the latter cases, there is an intention to relate theory to experiment at a rather sophisticated level. In solids, such high-resolution techniques are used to probe a range of other dynamic processes than the natural decay rate. For example, hole-burning may be induced by photochemical processes as well as by intrinsic lifetime processes.\(^2\)\(^3\)\(^M\) Such photochemical hole-burning processes have potential in optical information storage systems. OHB and FLN may also be used to study distortions in the neighborhood of defects. Figure 8 is an example of Stark spectroscopy and OHB on a zero-phonon line at 607 nm in irradiated NaF.\(^2\)\(^4\) This line had been attributed to an aggregate of four \( F \)-centers in nearest-neighbor
anion sites in the rocksalt-structured lattice on the basis of the polarized absorption/emission measurements. The homogeneous width in zero electric field was only 21 MHz in comparison with the inhomogeneous width of 3 GHz. Interpretation of these results is inconsistent with the four-defect model.

The FLN technique may also be used to measure the effects of phonon-induced relaxation processes and isotope shifts. Isotope and thermal shifts have been reported for Cr$^{3+}$: Al$_2$O$_3$ and Nd$^{3+}$: LaCl$_3$. The example given in Fig. 9 shows both the splitting in the ground $^4A_2$ state of Cr$^{3+}$ in ruby and the shift between lines due to the Cr(50), Cr(52), Cr(53), and Cr(54) isotopes. The measured differential isotope shift of 0.12 cm$^{-1}$ is very close to the theoretical estimate. Superhyperfine effects by the 100 percent abundant Al isotope with $I=5/2$ also contribute to the homogeneous width of the FLN spectrum of Cr$^{3+}$ in Al$_2$O$_3$ (Fig. 12 in Vol. I, Chap. 8, “Optical Spectroscopy and Spectroscopic Lineshapes”). Furthermore, in antiferromagnetic oxides such as GdAlO$_3$, Gd$_3$Ga$_5$O$_{12}$, and Gd$_3$Sc$_2$Ga$_3$O$_{12}$, spin-spin coupling between the Cr$^{3+}$ ions ($S=3/2$) and nearest-neighbor Gd$^{3+}$ ions ($S=3/2$) contributes as much to the zero-phonon R-linewidth as inhomogeneous broadening by strain.

### Configurational Relaxation in Solids

In the case of the broadband $^4T_2 \rightarrow ^4A_2$ transition of Cr$^{3+}$ in YAG (Fig. 12 — Optical Spectroscopy and Spectroscopic Lineshapes) and MgO (Fig. 6), the application of OHB
and FLN techniques produce no such narrowing because the vibronic sideband is the homogeneously broadened shape determined by the phonon lifetime rather than the radiative lifetime. It is noteworthy that the vibronic sideband emission of Cr\(^{3+}\) ions in orthorhombic sites in MgO, Fig. 10, shows very little structure. In this case, the Huang-Rhys factor $S = 6$, i.e., the strong coupling case, where the multiphonon sidebands tend to lose their separate identities to give a smooth bandshape on the lower-energy side of the peak. By way of contrast, the emission sideband of the $R$-line transition of Cr\(^{3+}\) ions in octahedral sites in MgO is very similar in shape to the known density of one-phonon vibrational modes of MgO\(^{39}\) (Fig. 11), although there is a difference in the precise positions of the peaks, because the Cr\(^{3+}\) ion modifies the lattice vibrations in its neighborhood relative to those of the perfect crystal. Furthermore, there is little evidence in Fig. 11 of higher-order sidebands which justifies treating the MgO $R$-line process in the weak coupling limit. The absence of such sidebands suggests that $S < 1$, as the earlier discussion in “Optical Spectroscopy and Spectroscopic Lineshapes” (Vol. I, Chap. 8 of this Handbook) showed. That the relative intensities of the zero-phonon line and broadband, which should be ca. $e^{-}$, is in the ratio $1:4$ shows that the sideband is induced by odd parity phonons. In this case it is partially electric-dipole in character, whereas the zero-phonon line is magnetic-dipole in character.\(^{19}\)

There has been much research on bandshapes of Cr\(^{3+}\)-doped spectra in many solids. This is also the situation for $F$-centers and related defects in the alkali halides. Here, conventional optical spectroscopy has sometimes been supplemented by laser Raman and sub-picosecond relaxation spectroscopies to give deep insights into the dynamics of the optical pumping cycle. The $F$-center in the alkali halides is a halide vacancy that traps an electron. The states of such a center are reminiscent of a particle in a finite potential well\(^{19}\) and strong electron-phonon coupling. Huang-Rhys factors in the range $S = 15–40$ lead to
broad, structureless absorption/luminescence bands with large Stokes shifts (see Vol. I, Chap. 8, Fig. 13). Raman-scattering measurements on F-centers in NaCl and KCl (Fig. 23 in Vol. II, Chap. 20, “Optical Spectrometers” in this Handbook), showed that the first-order scattering is predominantly due to defect-induced local modes.²⁰  

The $F_A$ center is a simple variant on the $F$-center in which one of the six nearest cation neighbors of the $F$-center is replaced by an alkali impurity.²¹ In KCl the $K^+$ may be replaced by Na or Li. For the case of the Na substituent, the $F_A$(Na) center has tetragonal symmetry about a $<100>$ crystal axis, whereas in the case of Li an off-axis relaxation in the excited state leads to interesting polarized absorption/emission characteristics.¹⁹,²¹ The most dramatic effect is the enormous Stokes shift between absorption and emission bands, of order 13,000 cm⁻¹, which has been used to advantage in color center lasers.²²,²³ For $F_A$(Li) centers, configurational relaxation has been probed using picosecond relaxation and Raman-scattering measurements. Mollenauer et al.⁴⁴ used the experimental system shown in this Handbook, (Vol. II, Chap. 20, Fig. 10), to carry out measurements of the configurational relaxation time of $F_A$(Li) centers in KCl. During deexcitation many phonons are excited in the localized modes coupled to the electronic states which must be dissipated into the continuum of lattice modes. Measurement of the relaxation time constitutes a probe of possible phonon damping. A mode-locked dye laser producing pulses of 0.7-ps duration at 612 nm was used both to pump the center in the $F_A$-absorption band and to provide the timing beam. Such pumping leads to optical gain in the luminescence band and prepares the centers in their relaxed state. The probe beam, collinear with the pump beam, is generated by a CW $F_A$(Li)-center laser operating at 2.62 µm. The probe beam and gated pulses from the dye laser are mixed in a nonlinear optical crystal (lithium iodate). A filter allows only the sum frequency at 496 nm to be detected. The photomultiplier tube then measures the rise in intensity of the probe beam which signals the appearance of gain where the $F_A$(Li)-centers have reached the relaxed excited state. The pump beam is chopped at low frequency to permit phase-sensitive detection. The temporal evolution of $F_A$(Li)-center gains (Figs. 12a and b) was measured
by varying the time delay between pump and gating pulses. In this figure, the solid line is the instantaneous response of the system, whereas in \( b \) the dashed line is the instantaneous response convolved with a 1.0-ps rise time.

Measurements of the temperature dependence of the relaxation times of \( F_{\alpha}(\text{Li}) \)-in potassium chloride (Fig. 12c) show that the process is very fast, typically of order 10 ps at 4 K. Furthermore, configurational relaxation is a multiphonon process which involves mainly the creation of some 20 low-energy phonons of energy \( E_P/\hbar c = 47 \text{ cm}^{-1} \). That only \( (20 \times 47/8066) \text{ eV} = 0.1 \text{ eV} \) is deposited into the 47 cm\(^{-1} \) mode, whereas 1.6 eV of optical energy is lost to the overall relaxation process, indicates that other higher-energy modes of vibrations must be involved.\(^{45} \) This problem is resolved by Raman-scattering experiments. For \( F_{\alpha}(\text{Li}) \)-centers in potassium chloride, three sharp Raman-active local modes were observed with energies of 47 cm\(^{-1} \), 216 cm\(^{-1} \), and 266 cm\(^{-1} \), for the \(^7\text{Li} \) isotope.\(^ {46} \) These results and later polarized absorption/luminescence studies indicated that the Li\(^+ \) ion lies in an off-center position in a (110) crystal direction relative to the \( z \) axis of the \( F_{\alpha} \)-center. Detailed polarized Raman spectroscopy resonant and nonresonant with the

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**FIGURE 12** (a) Temporal evolution of gain in the \( F_{\alpha}(\text{Li}) \) center emission in picosecond pulse-probe measurements, and (b) the temperature-dependence of the gain process. (After Mollenauer et al.)\(^44 \)
FIGURE 13 The Raman spectra of $F_A$-$\text{(Li)}$-centers in potassium chloride measured at 10 K for different senses of polarization. In (a) the excitation wavelength $\lambda = 600$ nm is midway between the peaks of the $F_A$-bands; (b) $\lambda = 632.8$ nm is resonant with the $F_A^1$ band, and (c) $\lambda = 676.4$ nm is nonresonant. (After Joosen et al.)

$F_A$-center absorption bands are shown in Fig. 13. These spectra show that under resonant excitation in the $F_A$ absorption band, each of the three lines due to the sharp localized modes is present in the spectrum. The polarization dependence confirms that the $266 \text{ cm}^{-1}$ mode is due to $\text{Li}^+$ ion motion in the mirror plane and parallel to the defect axis. The $216 \text{ cm}^{-1}$ mode is the stronger under nonresonant excitation, reflecting the off-axis vibrations of the $\text{Li}^+$ ion vibrating in the mirror plane perpendicular to the $z$ axis. On the other hand, the low-frequency mode is an amplified band mode of the center which hardly involves the motion of the $\text{Li}^+$ ion.
The philosophy of solid-state spectroscopy is subtly different from that of atomic and molecular spectroscopies. It is often required not only to determine the nature of the absorbing/emitting species but also the symmetry and structure of the local environment. Also involved is the interaction of the electronic center with other neighboring ions, which leads to lineshape effects as well as time-dependent phenomena. The consequence is that a combination of optical spectroscopic techniques may be used in concert. This general approach to optical spectroscopy of condensed matter phenomena is illustrated by reference to the case of Al$_2$O$_3$ and MgO doped with Cr$^{3+}$.

Absorption and Photoluminescence of Cr$^{3+}$ in Al$_2$O$_3$ and MgO

The absorption and luminescence spectra may be interpreted using the Tanabe-Sugano diagram shown in Fig. 5, as discussed previously. Generally, the optical absorption spectrum of Cr$^{3+}$:Al$_2$O$_3$ (Fig. 14) is dominated by broadband transitions from the $^4A_2\rightarrow^6T_2$ and $^4A_2\rightarrow^4T_1$. The crystal used in this measurement contained some $10^{18}$ Cr$^{3+}$ ions cm$^{-3}$. Since the absorption coefficient at the peak of the $^4A_2\rightarrow^6T_2$ band is only 2 cm$^{-1}$, it is evident from Eq. (6) in Chap. 20, “Optical Spectrometers”, in Vol. II of this Handbook, that the cross section at the band peak is $\sigma_0 \approx 5 \times 10^{-19}$ cm$^2$. The spin-forbidden absorption transitions $^4A_2\rightarrow^2E, ^2T_1$ are just distinguished as weak absorptions ($\sigma_0 \sim 10^{20}$ cm$^2$) on the long-wavelength side of the $^4A_2\rightarrow^6T_2$ band. This analysis strictly applies to the case of octahedral symmetry. Since the cation site in ruby is distorted from
perfect octahedral symmetry, there are additional electrostatic energy terms associated with this reduced symmetry. One result of this distortion, as illustrated in Fig. 14, is that the absorption and emission spectra are no longer optically isotropic. By measuring the peak shifts of the $^4A_2 \rightarrow ^4T_2$ and $^4A_2 \rightarrow ^4T_1$ absorption transitions between $\pi$ and $\sigma$ senses of polarization, the trigonal field splittings of the $^4T_2$ and $^4T_1$ levels may be determined.\(^{25}\)

The Cr\(^{3+}\) ion enters the MgO substitutionally for the Mg\(^{2+}\) ion. The charge imbalance requires that for every two impurity ions there must be one cation vacancy. At low-impurity concentrations, charge-compensating vacancies are mostly remote from the Cr\(^{3+}\) ions. However, some 10–20 percent of the vacancies occupy sites close to individual Cr\(^{3+}\) ions, thereby reducing the local symmetry from octahedral to tetragonal or orthorhombic.\(^{19}\) The optical absorption spectrum of Cr\(^{3+}\) : MgO is also dominated by broadband $^4A_2 \rightarrow ^4T_2$, $^4T_1$ transitions; in this case, there are overlapping contributions from Cr\(^{3+}\) ions in three different sites. There are substantial differences between the luminescence spectra of Cr\(^{3+}\) in the three different sites in MgO (Fig. 15), these overlapping

FIGURE 15 Showing photoluminescence spectra of Cr\(^{3+}\) : MgO using techniques of phase-sensitive detection. In (a) the most intense features are sharp $R$-lines near 698–705 nm due to Cr\(^{3+}\) ions at sites with octahedral and tetragonal symmetry; a weak broadband with peak at 740 nm is due to Cr\(^{3+}\) ions in sites of orthorhombic symmetry. By adjusting the phase-shift control on the lock-in amplifier (Fig. 4 in Vol. 2, Chap. 20 of this Handbook), the relative intensities of the three components may be adjusted as in parts (b) and (c).
spectra being determined by the ordering of the $^4T_2$ and $^2E$ excited states. For strong crystal fields, $Dq/B > 2.5$, $^2E$ lies lowest and nonradiative decay from $^4T_1$ and $^4T_2$ levels to $^2E$ results in very strong emission in the sharp $R$-lines, with rather weaker vibronic sidebands. This is the situation for Cr$^{3+}$ ions in octahedral and tetragonal sites in MgO.\textsuperscript{57} The $^2E \rightarrow {}^4A_2$ luminescence transition is both spin- and parity-forbidden (see this Handbook, Vol. I, Chap. 8) and this is signaled by relatively long radiative lifetimes—11.3 ms for octahedral sites and 8.5 ms for tetragonal sites at 77 K. This behavior is in contrast to that of Cr$^{3+}$ in orthorhombic sites, for which the $^4T_2$ level lies below the $^2E$ level. The stronger electron-phonon coupling for the $^4T_2 \rightarrow {}^4A_2$ transition at orthorhombic sites leads to a broadband luminescence with peak at 790 nm. Since this is a spin-allowed transition, the radiative lifetime is much shorter—only 35 µs.\textsuperscript{47}

As noted previously the decay time of the luminescence signals from Cr$^{3+}$ ions in octahedral and tetragonal symmetry are quite similar, and good separation of the associated $R$-lines using the phase-nulling technique are then difficult. However, as Fig. 15 shows, good separation of these signals from the $^4T_2 \rightarrow {}^4A_2$ broadband is very good. This follows from the applications of Eqs. (8)–(12) in this volume of the Handbook, Chap. 20. For Cr$^{3+}$ ions in cubic sites, the long lifetime corresponds to a signal phase angle of 28°: the $R$-line intensity can be suppressed by adjusting the detector phase angle to (90° + 2°). In contrast, the Cr$^{3+}$ ions in orthorhombic sites give rise to a phase angle of 85°; this signal is reduced to zero when $\phi_0 = (90° + 85°)$.

**Excitation Spectroscopy**

The precise positions of the $^4A_2 \rightarrow {}^4T_2$, $^4T_1$ absorption peaks corresponding to the sharp lines and broadband in Fig. 15 may be determined by excitation spectroscopy (see Vol. II, Chap. 20). An example of the application of this technique is given in Fig. 10, which shows the emission band of the $^4T_2 \rightarrow {}^4A_2$ transition at centers with orthorhombic symmetry, Figs. 10a and b, and its excitation spectrum, Fig. 10c.\textsuperscript{57} The latter was measured by setting the wavelength of the detection spectrometer at $\lambda = 790$ nm, i.e., the emission band peak, and scattering the excitation monochromator over the wavelength range 350–750 nm of the Xe lamp. Figure 10 gives an indication of the power of excitation spectroscopy in uncovering absorption bands not normally detectable under the much stronger absorptions from cubic and tetragonal centers. Another example is given in Fig. 16—in this case, of recombining excitons in the smaller gap material (GaAs) in GaAs/AlGaAs quantum wells. In this case, the exciton luminescence peak energy, $h\nu_0$, is given by

$$h\nu_0 = E_{1e} + E_{1h} + E_b$$

where $E_{1e}$ is the band gap of GaAs, $E_{1e}$, and $E_{1h}$ are the $n = 1$ state energies of electrons ($e$) and holes ($h$) in conduction and valence bands, respectively, and $E_b$ is the electron-hole binding energy. Optical transitions involving electrons and holes in these structures are subject to the $\Delta n = 0$ selection rule. In consequence, there is a range of different absorption transitions at energies above the bandgap. Due to the rapid relaxation of energy in levels with $n > 1$, the recombination luminescence occurs between the $n = 1$ electron and hole levels only, in this case at 782 nm. The excitation spectrum in which this luminescence is detected and excitation wavelength varied at wavelengths shorter than 782 nm reveals the presence of absorption transitions above the bandgap. The first absorption transition shown is the $1h \rightarrow 1e$ transition, which occurs at slightly longer wavelength than the $1h \rightarrow 1e$ transition. The light hole (lh)-heavy hole (hh) splitting is caused by spin-orbit splitting and strain in these epilayer structures. Other, weaker transitions are also discernible at higher photon energies.
Polarization Spectroscopy

The discussions on optical selection rules, in this Handbook in Vol. 1, Chap. 8 and Vol. II, Chap. 20, showed that when a well-defined axis is presented, the strength of optical transitions may depend strongly on polarization. In atomic physics, the physical axis is provided by an applied magnetic field (Zeeman effect) or an applied electric field (Stark effect). Polarization effects in solid-state spectroscopy may be used to give information about the site symmetry of optically active centers. The optical properties of octahedral crystals are normally isotropic. In this situation, the local symmetry of the center must be lower than octahedral so that advantage may be taken of the polarization-sensitivity of the selection rules (see, e.g., Vol. II, Chap. 20 of this Handbook). Several possibilities exist in noncubic crystals. If the local symmetry of all centers in the crystal point in the same direction, then the crystal as a whole displays an axis of symmetry. Sapphire (Al₂O₃) is an example, in which the Al³⁺ ions occupy trigonally distorted octahedral sites. In consequence, the optical absorption and luminescence spectra of ions in this crystal are naturally polarized. The observed π- and σ-polarized absorption spectra of ruby shown in Fig. 14 are in general agreement with the calculated selection rules, although there are undoubtedly vibronic processes contributing to these broadband intensities. The other important ingredient in the spectroscopy of the Cr³⁺ ions in orthorhombic symmetry sites in MgO is that the absorption and luminescence spectra are strongly polarized. It is then...
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FIGURE 17 The polarization characteristics of the luminescence spectrum of Cr\(^{3+}\) ions in orthorhombic sites in Cr\(^{3+}\): MgO. (After Henry et al.)

quite instructive to indicate how the techniques of polarized absorption/luminescence help to determine the symmetry axes of the dipole transitions. The polarization of the \(^5\)T\(_2\) \(\rightarrow\) \(^4\)A\(_2\) emission transition in Fig. 10 is clear. In measurements employing the “straight-through” geometry, Henry et al.\(^{47}\) report the orientation intensity patterns shown in Fig. 17 for the broadband spectrum. A formal calculation of the selection rules and the orientation dependence of the intensities shows that the intensity at angle \(\theta\) is given by

\[
I(\theta) = (A_\pi - A_\sigma)(E_\pi - E_\sigma) \sin^2 \left(\theta + \frac{\pi}{4}\right) + \text{constant}
\]

where \(A\) and \(E\) refer to the absorbed and emitted intensities for \(\pi\)- and \(\sigma\)-polarizations.\(^{48}\) The results in Fig. 17 are consistent with the dipoles being aligned along \((110)\) directions of the octahedral MgO lattice. This is in accord with the model of the structure of the Cr\(^{3+}\) ions in orthorhombic symmetry, which locates the vacancy in the nearest neighbor cation site relative to the Cr\(^{3+}\) ion along a \((110)\) direction.

**Zeeman spectroscopy**

The Zeeman effect is the splitting of optical lines by a static magnetic field due to the removal of the spin degeneracy of levels involved in the optical transitions. In many situations the splittings are not much larger than the optical linewidth of zero-phonon lines and much less than the width of vibronically broadened bands. The technique of optically detected magnetic resonance (ODMR) is then used to measure the Zeeman splittings. As we have already shown, ODMR also has the combined ability to link inextricably, an excited-state ESR spectrum with an absorption band and a luminescence band. The spectrum (Fig. 16 in Vol. II, Chap. 20 of this Handbook) is an example of this unique power, which has been used in such diverse situations as color centers, transition-metal ions, rare-earth ions, phosphor- and laser-active ions (e.g., Ga\(^{3+}\), Tl\(^{3+}\)), as well as donor-acceptor and exciton recombination in semiconductors.\(^{19}\) We conclude this review by illustrating the relationship of the selection rules and polarization properties of the triplet-singlet transitions.

The \(F\)-center in calcium oxide consists of two electrons trapped in the Coulomb field of
a negative-ion vacancy. The ground state is a spin singlet, $^1A_{1g}$, from which electric dipole absorption transitions are allowed into a $^3T_{1u}$ state derived from the $(1s2p)$ configuration. Such $^1A_{1g} \rightarrow ^3T_{1u}$ transitions are signified by a strong optical absorption band centered at a wavelength $\lambda = 400$ nm (Vol. II, Chap. 20, Fig. 16). De-excitation of this $^3T_{1u}$ state does not proceed via $^3T_{1u} \rightarrow ^1A_{1g}$ luminescence. Instead, there is efficient nonradiative decay from $^3T_{1u}$ into the triplet $^3T_{1u}$ state also derived from the $(1s2p)$ configuration (Henderson et al., 1969). The spin-forbidden $^3T_{1u} \rightarrow ^1A_{1g}$ transition gives rise to a striking orange fluorescence, which occurs with a radiative lifetime $\tau_R = 3.4$ ms at 4.2 K. The ODMR spectrum of the $F$-center and its absorption and emission spectral dependences were depicted in Fig. 16 in Chap. 20, “Optical Spectrometers” in Vol. II of this Handbook; other details are shown in Fig. 18. With the magnetic field at some general orientation in the (100) plane there are six lines. From the variation of the resonant fields with the orientation of the magnetic field in the crystal, Edel et al. (1972) identified the spectrum with the $S=1$ state of tetragonally distorted $F$-center. The measured orientation dependence gives $g_i = g_i' = 1.999$ and $D = 60.5$ mT.

Figure 18 shows the selection rules for emission of circularly polarized light by $S=1$ states in axial crystal fields. We denote the populations of the $M_s = 0, \pm 1$ levels as $N_0$ and $N_{\pm 1}$. The low-field ESR line, corresponding to the $M_s = 0 \rightarrow M_s = +1$ transition, should be observed as an increase in $\sigma_+\text{-light}$ because $N_0 > N_{+1}$ and ESR transitions enhance the

![Figure 18](image-url)
$M_s = \pm 1$ level. However, the high-field line is observed as a change in intensity of $\sigma^+$-light. If spin-lattice relaxation is efficient (i.e., $T_1 < \tau_R$), then the spin states are in thermal equilibrium, $N_\downarrow < N_\uparrow$, and ESR transitions depopulate the $|M_s = -1\rangle$ level. Thus, the high-field ODMR line is seen as a decrease in the $F$-center in these crystals (viz., that for the lowest $^3T_1$ state, $D$ is positive and the spin states are in thermal equilibrium). It is worth noting that since the $|M_s = 0\rangle \rightarrow |M_s = \pm 1\rangle$ ESR transitions occur at different values of the magnetic field, ODMR may be detected simply as a change in the emission intensity at resonance; it is not necessary to measure specifically the sense of polarization of the emitted light. The experimental data clearly establish the tetragonal symmetry of the $F$-center in calcium oxide: the tetragonal distortion occurs in the excited $^3T_1 u$ state due to vibronic coupling to modes of $E_g$ symmetry resulting in a static Jahn-Teller effect.

28.6 REFERENCES

2. D. N. Stacey, private communication to A. I. Ferguson.


