# Absorption Bands in the Spectra of Stars; A Crystal Field Approach

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## 1 Introduction

There has been a growing realization in recent years that important events occur in space between stars just as much as within stars. This realization has been stimulated by the discovery since 1968 of emission lines in the microwave region of the spectrum characteristic of about 39 polyatomic molecules,[1] the largest of which, recently discovered, is ethyl alcohol. Some workers believe that the organic precursors to life on Earth were present in the nebula from which the solar system condensed. The detection of polyatomic molecules came as a surprise to astronomers because the rate of destruction by photolysis in space is probably orders of magnitude greater than the rate of formation through two-body radiative and three-body collisions. The molecules are associated with dust clouds,[1,2] hence the reason for current belief that interstellar grains provide surfaces on which the molecules are formed and at the same time shield them from radiation. Transition-metals and their oxides are important Fischer–Tropsch catalysts for the production of hydrocarbons, aldehydes, and alcohols, and grains of iron and its oxides probably play an important role in the enrichment of meteorites and of interstellar space with organic molecules.[3] An understanding of the process by which these molecules are formed, therefore, requires a knowledge of the composition of the grains.

Light from distant stars is scattered and reddened by the fine particles that exist in interstellar space. Although many high-quality spectral data have been accumulated over the past 40 years or so, the composition of the dust remains conjectural.[4] Clouds of gas and of dust are evident to the naked eye in the extensive dark patches that occur in the Milky Way. The average extinction coefficient at 450 nm of dust near the galactic plane is *ca.* 1 magnitude per kilo-

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[1] D. M. Rank, C. H. Townes, and W. J. Welch, *Science*, 1971, **174**, 1083; E. Herbst and W. Klemperer, *Phys. Today*, 1976, **29**, 32.

[2] B. J. Bok, *Sci. Amer.*, 1972, **227**, 49.

[3] A. Brecher and G. Arrhenius, *Nature Phys. Sci.*, 1971, **230**, 107; M. H. Studier, R. Hayatsu, and E. Anders, *Geochim. Cosmochim. Acta*, 1968, **32**, 454.

[4] P. A. Annestad and E. M. Purcell, *Ann. Rev. Astron. Astrophys.*, 1973, **11**, 309; B. T. Lynds and N. C. Wickramasinghe, *Ann. Rev. Astron. Astrophys.*, 1968, **6**, 215; N. C. Wickramasinghe, 'Interstellar Grains', Chapman and Hall, London, 1967; N. C. Wickramasinghe and K. Nandy, *Reports Progr. Phys.*, 1972, **35**, 157; C. Wu, *Astrophys. J.*, 1972, **178**, 681; G. Carruthers, *Astrophys. Space Sci.*, 1971, **14**, 332.

parsec (1 mag kpc$^{-1}$), where 1 kpc $= 3 \times 10^{21}$ cm. The clouds are typically 0.03 kpc across and contain enough gas to form $10^5$ stars. Dust, as particles of radii $< 1 \mu$m, is a minor component of the clouds, but its presence shows up in the reddening and polarization of starlight. Several specialized reviews on the scattering and absorption properties of grains and on the use of electronic imaging devices have been published in the past decade.[4]

Apart from a few thermodynamic calculations on the condensation of solids in stellar atmospheres, almost all information on interstellar dust has been derived from the interaction of grains with electromagnetic radiation in the i.r. (3000 and 10 000 nm), visible, and u.v. ($\lambda > 110$ nm) regions. Important clues to the compositions of the grains are hidden in the diffuse interstellar absorption bands, which are observed in the visible-region spectra of reddened stars. It is to the interpretation of these bands that several workers have made recourse to crystal-field theory. The crystal-field approach, more so than any other, has shown promise in explaining the spectral characteristics of several of the broader and more prominent diffuse bands. This approach also provides a useful vehicle for bringing an important problem in astrochemistry to the attention of solid-state chemists. Other spectroscopic methods of studying dust are described briefly.

The interpretation of stellar spectra is dependent on wavelength coincidences between stellar absorption bands and bands measured in laboratory spectra of terrestrial solids. This is obviously a perilous approach, particularly where single broad absorptions are concerned, as is the case with the 217.5 nm ultraviolet and 10 000 nm infrared bands. On the other hand, the three dozen or so diffuse interstellar bands offer a greater opportunity for deriving a unique solution. All models must, ultimately, be assessed against the cosmic abundances of the elements (Table 1). These abundances, considered in conjunction with the

**Table 1** *Relative cosmic (interstellar) abundances$^a$ of the major elements* (Si $\equiv$ 1.0)

| Element | Abundance | Element | Abundance |
|---------|-----------|---------|-----------|
| H | 26 000 | Mg | 1.05 |
| O | 24 | Si | 1.0 |
| C | 13.5 | Fe | 0.9 |
| N | 2.4 | Al | 0.08 |

$^a$ A. G. W. Cameron, in 'Origin and Distribution of the Elements', ed. L. H. Ahrens Pergamon Press, 1968. These abundances are calculated on the assumption that the composition of the outer layers of the sun is similar to that of the interstellar cloud from which it condensed. Other abundances: Ti, V, Cr, Mn, Co, and Cu *ca.* 1% or less of Fe abundance.

estimated density of interstellar matter, $3 \times 10^{-24}$ g cm$^{-3}$, indicate that any model requiring, *e.g.*, an Fe density greater than $0.6 \times 10^{-26}$ g cm$^{-3}$, say by a factor of five, must be seriously questioned.

Polarized optical-absorption spectra have yielded considerable information on the electronic processes occurring in transition-metal-bearing silicate and oxide minerals, and in particular on next-nearest neighbour interactions. The diffuse

interstellar spectra are usually compared with absorptions in minerals and this custom is adopted here. For details of the recording of stellar spectra, the reader is referred to Wu,[4] and references therein, and to Carruthers.[4]

The following nomenclature is used. Astronomical distances are in parsecs (pc), where 1 pc = 3 light years = $3 \times 10^{18}$ cm. The positions of bands in spectra are given in the text in nm, although $cm^{-1}$, $\mu m^{-1}$, $\mu m$, and Å are used variously by chemists and astronomers. Stellar magnitudes and intensities ($I$) are related, for two stars A and B, by mag A − mag B = $-2.5 \log(I_A/I_B)$. Extinction coefficients ($\epsilon$) of bands are calculated from net band absorbance divided by the product of the cation concentration (in mol $l^{-1}$) and sample thickness (in cm).

## 2 Astronomical Observations

**A. Interstellar Extinction Curves.**—Extinction curves describe the wavelength dependence of scattering and of absorption by interstellar dust grains.[4] The curves are obtained by measuring the intensity difference in light received from a reddened star and from an unreddened star of the same spectral type, *i.e.* from two stars which have the same intrinsic spectrum of energy distribution with wavelength. Curves for several stars are shown in Figure 1.

Radiant energy is removed from starlight by absorption and by scattering. Cross-sections for absorption, scattering, and extinction are computed from the Mie formulae.[4,5] Considerable effort has been expended in reproducing the interstellar extinction curves over the wavelength range 3300—110 nm (3000—90 000 $cm^{-1}$) using laboratory-determined wavelength-dependent refractive indices of compounds thought likely to be abundant in interstellar space. Extinction curves have the following important features:

(*a*) Significant differences in the u.v. region occur for different stars, indicating that extinction is caused by a mixture of grains. A model of three components is favoured:[6] (i) dielectric particles of radii *ca.* 0.1 $\mu m$ to account for extinction in the 1000—300 nm range, (ii) small dielectric particles of radii ≪ 0.1 $\mu m$, possibly silicate, to account for far-ultraviolet extinction, and (iii) absorption by a solid, possibly graphite or silicate, to explain the hump at 217.5 nm.

(*b*) Extinction in the visible region is proportional to (wavelength)$^{-1}$. This compares with the (wavelength)$^{-4}$ law for Rayleigh scattering by small molecules.

(*c*) The broad hump at 217.5 nm (46 000 $cm^{-1}$) is commonly attributed to collective plasma oscillations in graphite.[7,8] These transitions involve the delocalized electrons and do not therefore occur in amorphous and vitrified forms of carbon. Wickramasinghe and co-workers have fitted the curves with a mixture of graphite, iron, and silicate particles of radii 0.05, 0.02, and 0.16 $\mu m$, respec-

[5] G. Mie, *Ann. Phys. Leipzig*, 1908, **25**, 377.
[6] J. M. Greenberg, in 'Interstellar Dust and Related Topics', ed. J. M. Greenberg and H. C. van de Hulst, Internat. Astron. Union, 1973, p. 3.
[7] D. P. Gilra, *Nature*, 1971, **229**, 237.
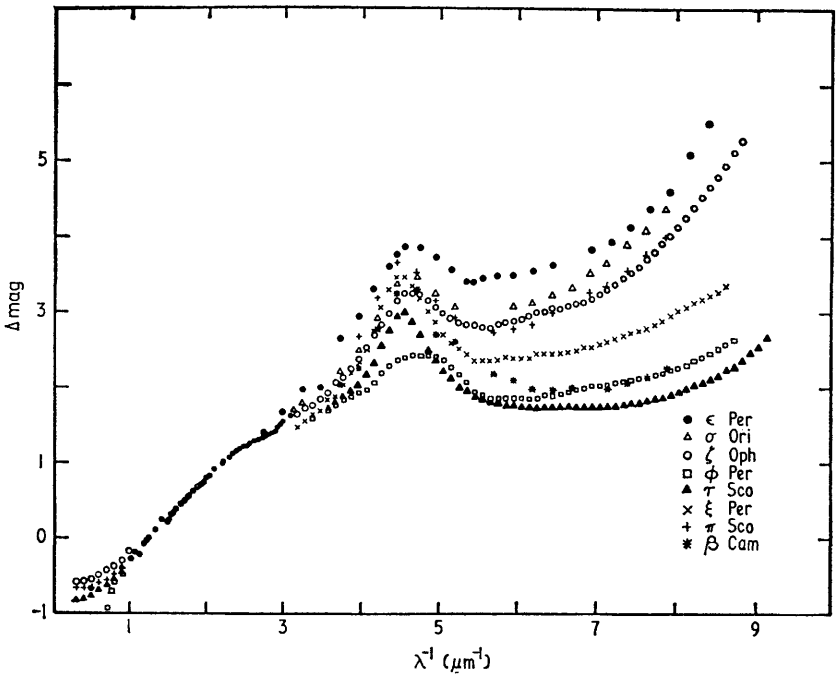[8] R. F. Willis, B. Feuerbacher, and B. Fitton, ref. 7, p. 303.

**Figure 1** *Extinction data[9] for several stars of the constellations Perseus, Orion, Ophiuchius, Scorpio, and Cameleopardus. Normalization is to Δ mag = 0 at λ⁻¹ = 1.22 μm⁻¹ (820 nm) and Δ mag = 1.0 at λ⁻¹ = 2.2 μm⁻¹ (455 nm)*. Data collated by Wickramasinghe and Nandy[4]
(Reproduced by permission from *Reports Progr. Phys.*, 1972, **35**, 157)

tively.[10] However, the hump profile is best reproduced with graphite grains that are of radius 0.02 μm, are spherical, and uncoated (with solid $H_2$, CO, *etc.*).[7] The restrictions placed on size and shape of the graphite particles causes particular concern. Other mixed-grain models proposed include graphite–SiC–silicate,[7] graphite–benzene,[11] and enstatite–iron.[12] In the absence of additional information, say, from the diffuse interstellar spectra or from polarization measurements, a unique solution to the extinction curve will prove difficult to obtain.

(*d*) The curve in the visible region can be approximated by two straight lines

[9] T. P. Stecher, *Astrophys. J.*, 1965, **142**, 1683; B. C. Bless and B. D. Savage, in 'Ultraviolet Stellar Spectra and Ground-based Observations', ed. L. Houziaux and H. E. Butler, Reidel, Dordrecht, 1970.
[10] N. C. Wickramasinghe and K. Nandy, *Nature*, 1970, **227**, 51; N. C. Wickramasinghe and K. Nandy, *Monthly Notices Roy. Astron. Soc.*, 1971, **153**, 205; K. Nandy and N. C. Wickramasinghe, *Monthly Notices Roy. Astron Soc*, 1971, **154**, 255.
[11] W. R. M. Graham and W. W. Duley, *Nature Phys. Sci.*, 1971, **232**, 43.
[12] D. R. Huffman and J. L. Stapp, *Nature Phys. Sci.*, 1971, **229**, 46

intersecting at *ca.* 435 nm (23 000 cm⁻¹).[13] The structure of the 'corner' in this region is uncertain, but it probably contains broad absorptions. An emission feature at *ca.* 555 nm in one composite reddening curve has been interpreted[14] as a dip lying between absorptions centred at *ca.* 670 and *ca.* 420 nm. A discontinuity has been observed at *ca.* 625 nm in other composite curves.[15] The band half-widths are *ca.* 2000 cm⁻¹, suggesting that they are of solid-state origin. The origin of these features is discussed in Section 3E.

**B. Infrared Spectra.**—The i.r. spectra of reddened stars reveal a broad feature at 10 μm, usually observed in emission.[16,17] The band has been attributed to silicate $Si - O$ stretching vibrations. Wavelength- and profile-matching with terrestrial silicates suggest an olivine. Silicates also absorb at *ca.* 20 μm, and increased stellar absorption has been observed at these wavelengths.[17] A band at *ca.* 3 μm was not detected in spectra of several moderately reddened stars and it now appears that $H_2O$-ice is a minor constituent of interstellar dust.[18] This ice band is prominent in spectra of one star in Orion.[18] Wickramasinghe has attributed the 3, 10, and *ca.* 20 μm absorptions to polyoxymethylene formed by the polymerization of formaldehyde on grains at *ca.* 20 K.[19] However, wavelength and band-profile coincidences are not convincing.

**C. Diffuse Interstellar Bands (DIB's).**—The spectra of distant stars comprise, in addition to well-identified sharp lines attributable to interstellar gas, several relatively broad diffuse absorption bands that are of as yet unknown origin.[20] They occur as fine structure on the interstellar extinction curve. Several were discovered by Merrill in 1936[21] and with subsequent discoveries they now total approximately three dozen. Profiles of some of the broader and, in terms of solid-state interactions, more interesting bands are shown in Figure 2. Wavelengths, energies, and half-widths of the broader features are listed in Table 2. The following aspects of the DIB's are important:

(*a*) DIB intensities are often correlated with general interstellar extinction,[22,23] suggesting that the bands are associated with grains.

[13] (*a*) K. Nandy, *Publ. Roy. Obs. Edinburgh*, 1964, **3**, 142; (*b*) *ibid.*, 1965, **5**, 13; J. W. Harris, *Nature*, 1969, **223**, 1046.
[14] D. S. Hayes, G. E. Marko, R. R. Radick, K. H. Rex, and J. M. Greenberg, ref. 7, p. 3.
[15] D. C. B. Whittet, I. G. Van Breda, and K. Nandy, *Nature Phys. Sci.*, 1973, **243**, 21; I. G. Van Breda, I. S. Glass, and D. C. B. Whittet, *Monthly Notices Roy. Astron. Soc.*, 1974, **168**, 551; P. G. Manning, *Nature*, 1975, **255**, 40.
[16] R. F. Knacke, J. E. Gausted, F. C. Gillett, and W. A. Stein, *Astrophys. J. Letters*, 1969, **155**, L189; F. C. Gillett and W. J. Forrest., *Astrophys. J.*, 1973 **179**, 483.
[17] J. A. Hackwell, R. D. Gehrz, and N. J. Woolf, *Nature*, 1970, **227**, 822.
[18] R. F. Knacke, D. D. Cudaback, and J. E. Gaustad, *Astrophys. J.*, 1969, **158**, 151.
[19] N. C. Wickramasinghe, *Nature*, 1974, **252**, 462.
[20] G. H. Herbig, in 'Interstellar Dust and Related Topics', Internat. Astron. Union Symposium No. 31, Academic Press, London and New York, 1967, p. 91.
[21] P. W. Merrill, *Astrophys. J.*, 1936, **33**, 136.
[22] E. J. Wampler, *Astrophys. J.*, 1966, **144**, 921; S. A. Kellman, *Publ. Astron. Soc. Pacific*, 1970, **82**, 1368.
[23] G. H. Herbig, *Z. Astrophys.*, 1966, **64**, 512; *Astrophys. J.*, 1975, **196**, 129.
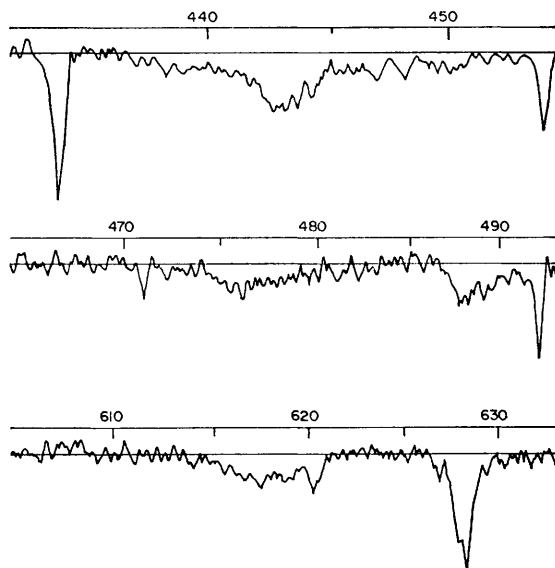
**Figure 2** *Intensity tracings of the spectrum of the star* HD183143, *showing the broad interstellar bands at* 443, 476, 489, *and* 618 nm[24]
(Reproduced by permission from *Astrophys. J.*, 1958, **128**, 57)

**Table 2** *Wavelengths and half-widths of strongest diffuse interstellar bands[a,b]*

| Wavelength (*band centre*) | Half-width | |
|---|---|---|
| nm | nm | cm$^{-1}$ |
| 443 | 2.8 | 150 |
| 476 | 3.0 | 130 |
| 489 | 3.0 | 130 |
| 577.8 | 1.7 | 50 |
| 578.0 | 0.4 | 10 |
| 618 | 3.0 | 80 |
| 628 | 0.4 | 10 |
| 661 | 0.2 | 5 |

[a] Several of the weaker bands have half-widths of *ca.* 0.1 nm.  [b] N. C. Wickramasinghe and K. Nandy, *Reports Progr. Phys.*, 1972, **35**, 157.

(*b*) The peak position of the 443 nm band is constant to within 0.1 nm for several stars.[23] No fine structure has been seen in the 443 nm band of two stars down to a scale of 0.015 nm, showing that the band is not caused by free molecules. Suggestions that the band is caused by the pre-ionization of negative ions like H$^-$ are now discounted.[25]

[24] R. Wilson, *Astrophys. J.*, 1958, **128**, 57.
[25] G. Herzberg, *Mem. Soc. roy. Sci. Liège*, 1955, **15**, 291; E. Herbst, T. A. Patterson, and D. W Norcross, *Astrophys J. Letters*, 1974, **191**, L143.

(*c*) The relative intensities of the bands are not necessarily constant, although the 443 nm band is usually the most prominent.

(*d*) All bands found so far, for some unknown reason, occur in the visible region of the spectrum. However, it has been proposed that one occurs in the near-u.v. at 368 nm (27 160 cm$^{-1}$).[26]

(*e*) The polarization of the DIB's is in dispute. Recent measurements indicate that the 443 nm band is polarized to about the same degree as the continuum on either side.[27] This suggests that the grains causing DIB's are not those responsible for general interstellar extinction.

(*f*) DIB intensities indicate that the absorbing ions are cosmically abundant. Rare-earth ions, for example, are unlikely candidates. Complex molecules such as Johnson's porphyrins[28] have some support among astronomers, but the main problem here is their liability to photo-dissociation (other disadvantages are discussed by Wu[4]).

In 1967—68 Wickramasinghe and co-workers proposed that the DIB's are caused by transitions within impurity ions in grains,[29] without proposing any one model. Two solid-state models were developed in the late 60's and early 70's: one attributes the bands to absorption lines of metal atoms embedded in solid hydrocarbons and the other to crystal-field transitions in ferric ions.

**D. Type-I Supernova Bands.**—In 1968 Seddon suggested that the optical spectra of Type-I supernovae, traditionally considered as comprising broad emission features on a darker continuum, could be thought of as absorption bands on a brighter continuum.[30] In well resolved spectra the wavelengths of four of the prominent absorptions are 443, 476, 489, and 618 nm, which are the DIB wavelengths.[31,32] The bands can then be attributed to material condensing out of the expanding supernova shell. Another important band occurs at 380 nm. Such events enrich space with dust. Duley and Graham noted wavelength coincidences between 11 supernova bands and absorptions observed in laboratory spectra of dispersions of Mg, Ca, Ti, and Na, in benzene or toluene.[33] The 443 nm supernova band, and by implication the 443 nm DIB, they assigned to Ca atoms trapped in solid benzene on grains. However, treating the supernova traces as absorption spectra is highly controversial,[34] and it is recommended that future solid-state work be concentrated on the analysis of DIB's.

[26] R. K. Honeycutt, *Astron. J.*, 1972, **77**, 24.
[27] P. G. Martin and J. R. P. Angel, *Astrophys. J.*, 1974, **188**, 517.
[28] F. M Johnson, *Mem. Soc. roy. Sci. Liège*, 1972, 391.
[29] N. C. Wickramasinghe, J. G. Ireland, K. Nandy, H. Seddon, and R. D. Wolstencroft, *Nature*, 1968, **217**, 412; F. Hoyle and N. C. Wickramasinghe, *Nature*, 1967, **214**, 969.
[30] H. Seddon, *Nature*, 1969, **222**, 757.
[31] M. Bloch, D. Chalonge, and J. Dufay, *Ann. d'Astrophys.*, 1964, **24**, 315.
[32] P. G. Manning, *Nature*, 1970, **227**, 1121.
[33] W. W. Duley and W. R. M. Graham, *Nature*, 1969, **224**, 785; W. R. M. Graham and W. W. Duley, *Nature Phys. Sci.*, 1971, **232**, 43.
[34] J. B. Oke and L. Searle, *Ann. Rev. Astron. Astrophys.*, 1974, **12**, 315.

## 3 Interpretation of the Diffuse Interstellar Bands

**A. Optical Absorption Spectra of Ferric Ions.**—Considerable progress has been made in recent years in gaining an understanding of the crystal-field spectra of ferric ions in solids. This is due in no small measure to the study of minerals. U.v.-centred charge-transfer absorption in silicates occurs at sufficiently short wavelengths that $Fe^{3+}$ crystal-field bands are often resolved to *ca*. 300 nm. The half-widths and intensities of $Fe^{3+}$ bands are sensitive to next-nearest neighbour interactions and are consequently useful probes of local crystal composition. Garnets will be considered here as representing much of the crystal chemistry of $Fe^{3+}$-bearing silicates. Garnets are cubic minerals of complex structure and composition.[35] The molecular formula is $M^1{}_6M^2{}_4M^3{}_6O_{24}$, where $M^1$ cations are in eight-co-ordination, $M^2$ in regular-octahedral co-ordination and $M^3$ in tetrahedral co-ordination. Important end-members are listed in Table 3, but the pure

**Table 3** *Cell-dimensions* (*a*) *and ideal compositions of naturally occurring garnet end-members*

| Garnet | $a/\text{Å}$ | $M^1$ | $M^2$ | $M^3$ | |
|---|---|---|---|---|---|
| Pyrope | 11.46 | $Mg^{2+}$ | Al | Si | ⎫ |
| Almandine | 11.53 | $Fe^{2+}$ | Al | Si | ⎬ pyralspites |
| Spessartine | 11.62 | $Mn^{2+}$ | Al | Si | ⎭ |
| | | | | | |
| Grossular | 11.85 | $Ca^{2+}$ | Al | Si | ⎫ |
| Uvarovite | 12.00 | $Ca^{2+}$ | $Cr^{3+}$ | Si | ⎬ ugrandites |
| Andradite | 12.05 | $Ca^{2+}$ | $Fe^{3+}$ | Si | ⎭ |

end-members do not exist in nature. For example, pyrope from its molecular formula should be colourless because MgO, $Al_2O_3$, and $SiO_2$ do not absorb in the visible region, but traces of $Cr^{3+}$ colour pyrope blood-red.[3] In contrast, uvarovite is a deep green, reflecting a longer $Cr-O$ distance and a weaker crystal-field.

A continuous series of solid solutions exists between end-members within each series but not extensively between members of different series. Ionic sizes play an important role in determining the solubility of cations. For example, the solubility of $Fe^{3+}$ is *ca*. 1 % by weight in tight sites in pyralspites $(Al-O$ distance 0.189 nm), *ca*. 5 % in grossulars $(Al-O$ 0.195 nm), and 20 % in andradite $(Fe-O$ 0.202 nm).[35] Appreciable amounts of Ti are soluble in the large andradite cell, but because $Ti^{4+}$ shows a marked preference for octahedral positions tervalent ions replace Si for charge neutralization. A much-studied schorlomite from Magnet Cove, Arkansas, has the approximate composition[36,37]

[35] W. A. Deer, R. A. Howie, and J. Zussman, 'Rock-forming Minerals', Longman, London, 1962.
[36] (*a*) R. A. Howie and A. R. Woolley, *Mining Mag.* (*London*), 1968, **36**, 775; (*b*) P. G. Manning, *Canad. Mineral.*, 1973, **12**, 120.
[37] P. G. Manning, unpublished results.

$Ca_6(Fe^{3+}_{1.9}Al_{0.1}Mg_{0.3}Ti^{4+}_{1.8})$ $(Si^{4+}_{4.5}Al^{3+}_{0.9}Fe^{3+}_{0.6})O_{24}$. In the garnet structure, each oxygen ion is bonded to two eight-co-ordinate cations (Ca), one octahedrally bonded cation, and one tetrahedrally bonded cation. Octahedral $Fe^{3+}$ ions have six next-nearest neighbour tetrahedral ions.

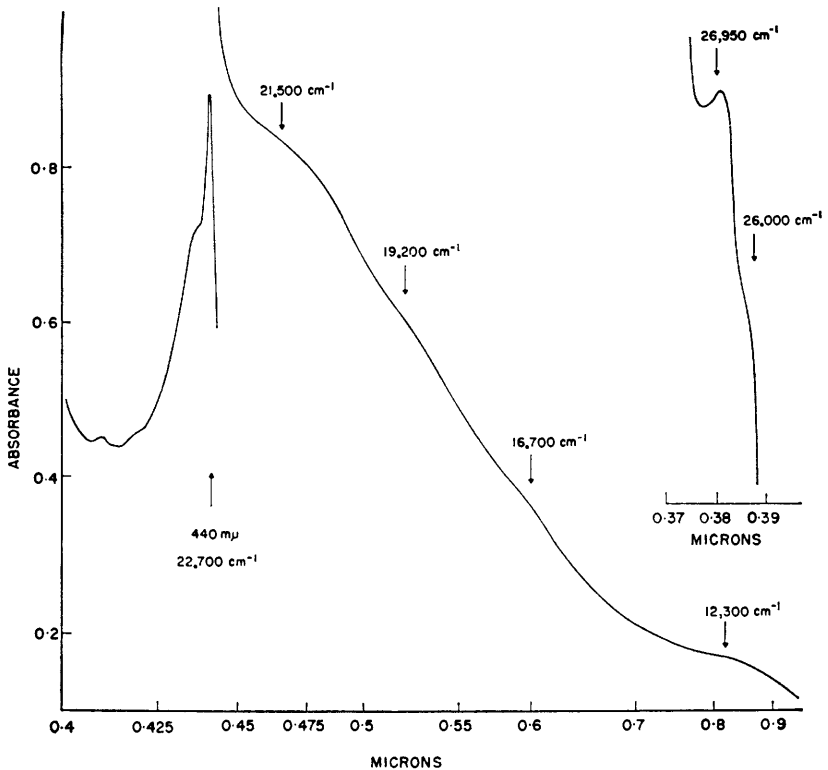The optical spectrum of an andradite in the visible region (Figure 3) is



**Figure 3** *Optical absorption spectrum of an andradite crystal of thickness* 0.2 mm. *Bands at* 19 200 *and* 21 700 $cm^{-1}$ *caused by impurity ions*
(Reproduced by permission from *Canad. Mineral.*, 1969, 9, 723)

dominated by a sharp two-component envelope (total half-width 450 $cm^{-1}$ or 8.5 nm at 300 K; $\epsilon$ = extinction coefficient = 1) centred at 440 nm (22 700 $cm^{-1}$), with weaker and broader absorptions at 600 nm (half-width 72 nm; $\epsilon$ = 0.1) and 833 nm (half-width 80 nm; $\epsilon$ = 0.05).[38] A second relatively sharp band is observed at 370 nm, with a half-width of *ca*. 20 nm and an $\epsilon$-value of *ca*. 2. Oscillator strengths for the 600, 440, and 370 nm bands are, respectively, 1.5 ×

[38] P. G. Manning, *Canad. J. Earth Sci.*, 1967, **4**, 1039; R. K. Moore and W. B. White, *Canad. Mineral.*, 1972, **11**, 791.

$10^{-6}$, $3.5 \times 10^{-6}$, and $2 \times 10^{-5}$. The increasing intensities of the bands as their peak positions move to shorter wavelengths reflect intensity-stealing from oxygen→$Fe^{3+}$ u.v.-centred charge-transfer absorption ($\epsilon > 10^4$) through mixing of even-parity crystal-field states with odd-parity charge-transfer states.[39]

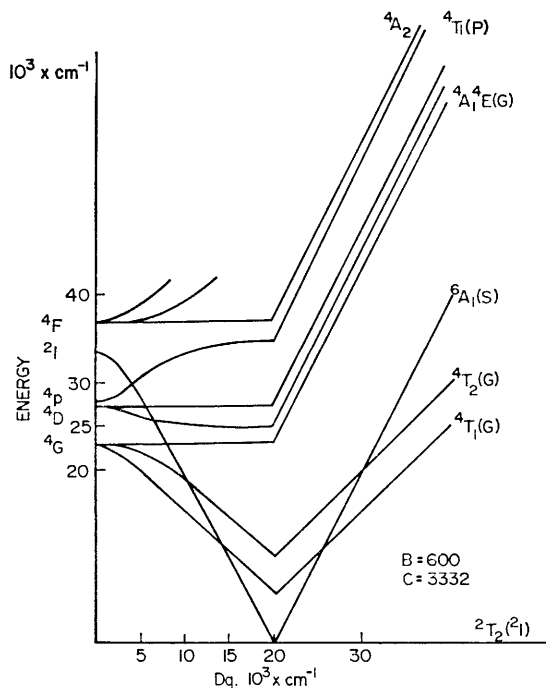An energy-level diagram for $Fe^{3+}$ in cubic fields is shown in Figure 4. The $^4A_1$



**Figure 4** *Energy level diagram for* $Fe^{3+}$ *ions in cubic fields.*[40] *Values of Racah B and C parameters are similar to those measured for* $Fe^{3+}$ *ions in andradite, for which the calculated value of* 10 *Dq is* 1350 cm$^{-1}$
(Reproduced by permission of the author)

and $^4E$ levels derived from the Russell–Saunders $G$ state and the $^4E$ level derived from the $D$ state are field-independent; hence transitions to these levels give rise to the sharpest absorption bands in the spectrum. The 440 nm envelope is assigned to the former transition, and this is confirmed by the two components which correspond to weakly split $^4A_1$ and $^4E$ levels. Other band assignments in andradite spectra are straightforward, and are listed in Table 4, together with assignments for $Fe^{3+}$ bands in spectra of several other minerals. Good-quality

[39] P. G. Manning and M. G. Townsend, *J. Phys.* (*C*), 1970, **3**, L14.
[40] J. S. Berkes, Monograph No. 2, Materials Research Laboratory, Pennsylvania State University, 1968.

spectra of tetrahedral $Fe^{3+}$ ions are more difficult to come by, but a listing of band assignments for this ion in terrestrial materials is given in Table 4. The $3d^5$ energy-level diagram shows that the weaker the crystal-field the closer in energy are transitions to the $^4T_1(G)$, $^4T_2(G)$, and $^4A_1^4E(G)$ levels. Tetrahedral fields are weaker than octahedral, and hence the assignments in Table 4 are not unreasonable.

**Table 4** *Wavelengths /nm of transitions in* $Fe^{3+}$ *ions in silicates and oxides and calculated values /$cm^{-1}$ of Racah B parameter*

| Material | Co-ordination* | $^4T_1(G)$ | $^4T_2(G)$ | $^4A_1\,^4E(G)$ | $^4E(D)$ | B | Ref. |
|---|---|---|---|---|---|---|---|
| Spessartine | 6 | — | — | 432, 422 | 372 | 500 | a |
| Grossular | 6 | 833 | 592 | 433 | 370 | 555 | a |
| Andradite | 6 | 833 | 600 | 435, 440 | 370 | 595 | a |
| Jadeite | 6 | 828 | 536 | 431, 437 | — | — | b |
| Aegerine | 6 | — | 600 | 433, 438 | 372 | 550 | c |
| Kyanite | 6 | — | — | 446, 428 | 370 | 585 | d |
| Corundum | 6 | 1060 | *ca.* 600 | 452 | 376 | 640 | e |
| Muscovite | 6 | 900 | 600 | 443 | 366 | 670 | a |
| Phosphate glass | 6 | 740 | 520 | 415 | — | — | f |
| Phlogopite | 4 | 520 | 483 | 440 | — | — | g |
| Orthoclase | 4 | — | 483 | 441, 416 | 378 | 550 | a |
| Silicate glass | 4 | 480 | 448 | *ca.* 425 | 370 | 550 | f |

[a] P. G. Manning, *Canad. Mineral.*, 1970, **10**, 677; [b] G. R. Rossman, *Amer. Mineralogist*, 1974, **59**, 868; [c] P. G. Manning and P. Lapointe, unpublished data; [d] G. H. Faye and E. H. Nickel, *Canad. Mineral.*, 1969, **10**, 35; [e] G. Lehmann and H. Harder, *Amer. Mineralogist*, 1970, **55**, 98; [f] C. R. Kurkjian and E. A. Sigety, *Phys. and Chem. Glasses*, 1968, **9**, 73; [g] G. H. Faye and D. D. Hogarth, *Canad. Mineral.*, 1969, **10**, 25.

* 6 = octahedral, 4 = tetrahedral.

In 1970 several workers independently drew attention to wavelength coincidences between the DIB's and absorption bands in spectra of terrestrial oxides (yttrium iron garnet and haematite, $\alpha$-$Fe_2O_3$) and Fe-bearing silicates.[32,41–43] It was further suggested that Type I supernova bands were of similar origin. Although he did not measure its spectrum, Huffman[42] favoured maghemite ($\gamma$-$Fe_2O_3$) as the insterstellar absorber on the grounds that the wavelengths of some of the DIB's match those of tetrahedral $Fe^{3+}$. Maghemite has a spinel structure containing octahedrally and tetrahedrally co-ordinated ferric ions. Laboratory studies show that water is required to form maghemite and water seems an integral part of the structure.[44] However, $H_2O$ as ice is not

[41] D. R. Huffman, *Nature*, 1970, **225**, 833; P. G. Manning, *Nature*, 1970, **226**, 929; J. Dorschner, *Astron. Nachr.*, 1970, **292**, 107.
[42] D. R. Huffman, *Astrophys. J.*, 1970, **161**, 1157.
[43] W. A. Runciman, *Nature*, 1970, **228**, 843.
[44] I. David and A. J. E. Welch, *Trans. Faraday Soc.*, 1956, **52**, 1142.

particularly abundant in space.[18] Maghemite is a metastable mineral which converts into haematite on heating to 500—800 K. Over millions of years interstellar dust is likely to be heated to these temperatures by, for example, close passage to stars and the flare-up of stars.

A second suggestion was that the DIB's are caused by a silicate such as schorlomite in which ferric ions in octahedral co-ordination have, as next-nearest neighbours, ferric ions in tetrahedral positions substituting for Si.[32] Both $O^2-2p \rightarrow Fe^{3+}3dt_2$ charge-transfer and $Fe^{3+}$ $d$–$d$ absorption are dramatically enhanced in schorlomite, and $\epsilon$-values for the 440 nm bands are 1 in andradite and *ca.* 25 in schorlomite.[36] The octahedral-$Fe^{3+}$ band at 600 nm is present in both spectra. Accordingly, the strongest DIB at 443 nm was assigned to the $A_1 \rightarrow {}^4A_1{}^4E(G)$ transition in octahedral ferric ions.[32,41] It follows that the 618, 476, and 4I9 nm DIB's can be assigned to transitions to the levels ${}^4T_2(G)$ in octahedral $Fe^{3+}$, and to ${}^4T_2(G)$ and to ${}^4T_1(G)$ in the tetrahedral ion, respectively. However, the silicate garnet theory has two important drawbacks. Firstly, garnets are formed under high pressures, in some cases corresponding to those in the Earth's mantle, and secondly, the cosmic abundance of Ti is too low to be compatible with schorlomite formation in large amounts (Table 1).

Runciman pointed out wavelength coincidences between DIB's and ferrous ion absorptions in silicates.[43] The transitions are from the ${}^5T_2(D)$ ground state to triplet states and are therefore spin-forbidden.[45] Extinction coefficients are *ca.* 0.1 and are considerably smaller ($\times 10^{-1}$) than for $Fe^{3+}$ $d$–$d$ bands. No single band in ferrous ion spectra dominates to the same extent as does the 440 nm band in ferric spectra. For these reasons ferric ions are favoured as the cause of the DIB's. Dorschner later criticized wavelength correlations on the grounds that transition-metal ions absorb as a group at innumerable wavelengths in the visible region,[46] and solutions to the diffuse interstellar spectra cannot therefore be unique. However, other transition-metal ions are considerably less abundant than Fe. The optical spectra of $Mn^{2+}(3d^5)$ ions are similar to those of $Fe^{3+}$, but $Mn^{2+}d$–$d$ bands are considerably less intense and Mn is two orders of magnitude less abundant than Fe. Additionally, $Ti^{3+}$ ions can be eliminated because the ${}^2T_2 \rightarrow {}^2E(D)$ crystal-field band in minerals is very broad (half-width 100 nm) and has no obvious counterpart in the DIB's.[47]

Because the $Fe^{3+}$ ${}^4A_1(G)$ and ${}^4E(G)$ levels are not exactly degenerate in terrestrial solids, it is anticipated that the 443 nm band should be asymmetric or should have a partner band up to 20 nm away. There is evidence that the 443 nm band in the spectra of several stars is steeper on the high-energy side.[48] Alternatively, a weak interstellar band is present at 450 nm.

**B. Interstellar Band Intensities and Iron Abundances.**—Because ferric $d$–$d$ bands are spin-forbidden and Laporte-forbidden and are therefore very weak, it

[45] P. G. Manning, *Nature*, 1970, **228**, 844.
[46] J. Dorschner, *Nature*, 1971, **231**, 124.
[47] P. G. Manning and D. C. Harris, *Canad. Mineral.*, 1970, **10**, 260.
[48] M. T. Bruck and K. Nandy, *Nature*, 1968, **220**, 46; G. E. Bromage, *Astrophys. Space Sci.*, 1972, **15**, 426

becomes important to determine whether iron is sufficiently abundant to account for the diffuse bands. The absorption of the 443 nm band is *ca.* 0.1 mag kpc$^{-1}$, corresponding to an absorbance of 0.04 kpc$^{-1}$. In the Magnet Cove schorlomite, in which iron–iron interactions are considered representative of silicates containing ferric ions in adjacent octahedral and tetrahedral positions, the concentration of octahedral ferric ions is 10.5% or 7.2 mol l$^{-1}$, and the $\epsilon$-value of the 440 nm band *ca.* 25. From these figures, the 'thickness' of schlorlomite along line of sight is 2.2 μm and the weight of a disc of 1 cm$^2$ cross-section is 8.4 × 10$^{-4}$ g. This is also the weight of material over 3 × 10$^{21}$ cm$^3$. The density of schorlomite in interstellar space is then 3 × 10$^{-25}$ g cm$^{-3}$ and that of Fe 4 × 10$^{-26}$ g cm$^{-3}$, which compares unfavourably with the accepted Fe density[42] of 0.6 × 10$^{-26}$ g cm$^{-3}$.

Huffman resolved the spectrum of a 12 μm section of haematite at energies up to *ca.* 650 nm, from which he was able to measure the absorbance of the 830 nm band marking the $Fe^{3+}$ $^4T_1(G)$ level.[42] Absorption by haematite is so intense that sections have not been prepared thinly enough to resolve the blue region of the spectrum. However, absorption at 440 nm has been observed in thin films of $Fe_2O_3$.[49] Huffman then assumed, as is generally justified from a knowledge of spectra of terrestrial materials, that the absorbance of the 443 nm band is ten times that of the 833 nm band. He calculated a $\gamma$-$Fe_2O_3$ density in space of 1.6 × 10$^{-26}$ g cm$^{-3}$.

An understanding of $Fe^{3+}$ interactions in solids that cause such widely different $\epsilon$-values for the $Fe^{3+}$ $^6A_1 \rightarrow$ $^4A_1$ $^4E(G)$ transition is of considerable importance because intensity considerations will eliminate many ferric compounds as candidates for the DIB's. Table 5 presents $\epsilon$-values, the colours of, and the degree of antiferromagnetic interaction in a number of $Fe^{3+}$-bearing solids.[36,50] The

**Table 5** *Colour, degree of antiferromagnetic interaction, and $\epsilon$-values for some ferric-bearing compounds*[a]

| Compound | Colour | Antiferromagnetism | $\epsilon(^4A_1{}^4E)$ |
|---|---|---|---|
| Phosphate | lavender | weak | |
| Sulphate | lavender | weak | |
| Grossular | green | weak | *ca.* 1 |
| Andradite | green | weak | |
| Schorlomite | black | | |
| Botryogen | orange | moderate | 25—100 |
| Magnesiocopiapite[b] | amber | | |
| Haematite | red | strong | *ca.* 500 |

[a] Data from ref. 50. [b] $MgFe_4(SO_4)_6(OH)_2,20H_2O$.

[49] R. C. Vernon, *J. Appl. Phys.*, 1962, **33**, 2140.
[50] G. R. Rossman, *Amer. Mineralogist*, 1975, **60**, 698.

substitutional effects described for schorlomite also occur in the clinopyroxene titanaugite, which has the approximate formula $Ca(Mg, Fe^{2+}, Fe^{3+}, Al)_1(Si_{2-x}, Al, \text{ or } Fe^{3+}_x)O_6$, where $x$ is commonly 0.3.[34,36] Each octahedrally bonded (Mg, Fe, Al) ion has six next-nearest neighbour tetrahedrally co-ordinated (Si, Al, Fe) ions. The absorption at 450 nm in titanaugite spectra is broad and comprises overlapping bands of $Fe^{3+}$ on octahedral and tetrahedral positions.[51,52] The average $\epsilon$-value for the octahedral-$Fe^{3+}$ bands is probably *ca.* 10. The structure of copiapite contains chains of ferric dimers bridged by an hydroxide ion and two sulphate tetrahedra; the effective magnetic moment per iron, $\mu = 4.70$ B.M., is lower than the 5.9 B.M. observed for magnetically dilute $Fe^{3+}$.[50] Botryogen, $MgFe(SO_4)_2(OH),7H_2O$, contains chains of hydroxo-bridged $Fe^{3+}$, and $\mu = 3.97$ B.M. Haematite and gadolinium iron garnet also show strong magnetic interactions. Ferric oxo-bridged dimers exist in $enH_2[(Fe\ Hedta)_2O],6H_2O$, and here also the crystal-field absorptions are relatively intense and antiferromagnetic interactions strong.[53] Clearly, normal selection rules break down in solids containing antiferromagnetically coupled ferric ions.[54] Alternatively, it has been suggested that the intensification of ferric ion $d$–$d$ transitions arises from intensity-stealing from oxygen → $Fe^{3+}$ charge-transfer processes.[36b] In schorlomite and titanaugite, the replacement of $Si^{4+}$ ions by larger less-covalently bonded $Fe^{3+}$ and $Al^{3+}$ ions has the effect of increasing electronic charge on the oxygens, making them more polarizable and promoting oxygen → octahedral-$Fe^{3+}$ charge-transfer. This substitutional process certainly enhances charge-transfer because sections of andradite and schorlomite must be thinned to thicknesses of, respectively, 0.02 cm and 0.0015 cm to permit resolution of the spectrum to 400 nm. While both intensity-stealing and spin–spin coupling processes are probably operative, Rossman's demonstration that the $^4A_1{}^4E(G)$ bands in spectra of magnesiocopiatite and botryogen are particularly intense for light vibrating parallel to the Fe–Fe axis suggests that antiferromagnetic coupling is more important. Another important feature of spin–spin coupled $Fe^{3+}$ (and $Mn^{2+}$) dimer systems is that a single photon can excite $d$–$d$ transition in the two ions simultaneously.[53,54] The energy of this double-ion transition is approximately equal to the sum of the energies of the single-ion transitions, and $\epsilon$-values are *ca.* 1500. An absorption is therefore anticipated at 221 nm in interstellar spectra (443/2). The intensities of the 217.5 nm feature and the 413 nm DIB are well correlated for over sixty stars,[55] suggesting that both absorptions arise from the same carrier or that the carriers co-exist in the interstellar medium. However, the 217.5 nm band seems too broad for the double-ion transition, and it probably 'swamps' any trace of the anticipated 221 nm band.

[51] P. G. Manning and E. H. Nickel, *Canad. Mineral.*, 1963, **10**, 71.
[52] R. G. Burns and F. E. Huggins, *Amer. Mineralogist*, 1973, **58**, 955.
[53] K. S. Murray, *Coordination Chem. Rev.*, 1974, **12**, 1.
[54] J. Ferguson and P. E. Fielding, *Austral. J. Chem.*, 1972, **25**, 1371; H. J. Schugar, G. R. Rossman, C. J. Barraclough, and H. B. Gray, *J. Amer. Chem. Soc.*, 1972, **94**, 2683.
[55] K. Nandy and G. I. Thompson, *Monthly Notices Roy. Astron. Soc.*, 1975, **173**, 237.

**C. Band Half-widths.**—The half-width of the two-component $^4A_1$ $^4E(G)$ envelope in spectra of andradite and spessartine is *ca.* 8 nm at 300 K and *ca.* 7 nm at 77 K. The corresponding half-widths in grossular and schorlomite spectra are in the 18—25 nm range (1000—1400 cm$^{-1}$), showing that these envelopes comprise two or three overlapping 8 nm wide sub-envelopes, the centres of which are separated by several hundred wavenumbers.[56] Each sub-envelope reflects ferric ions with different next-nearest neighbour compositions. Chemical analyses and Mössbauer studies of schorlomites show appreciable substitution of ferric ions into tetrahedral positions.[37,57] Often there is insufficient tetrahedral-ferric ion to make up the Si deficiency, and Al$^{3+}$ ions are also considered to replace Si. Tetrahedral-site compositions in the Magnet Cove schorlomite are 5Si + 1Fe$^{3+}$/Al$^{3+}$ and 4Si + 2Fe$^{3+}$/Al$^{3+}$, with smaller amounts of 6Si *etc.* Mössbauer spectra comprise a broad octahedral-Fe$^{3+}$ doublet and a narrow tetrahedral-ferric doublet. Mössbauer studies of several grossulars show that the octahedral-ferric peaks are considerably broad (half-widths 0.35—0.58 mm s$^{-1}$) than those in andradite (0.24 mm s$^{-1}$).[58] No measurable amounts of tetrahedral-Fe$^{3+}$ are observed ($< 2\%$ of total Fe). The $\epsilon$-value of the $^4A_1$ $^4E(G)$ octahedral-ferric band is 1 in grossular, showing there is no antiferromagnetic interaction in grossulars and that Fe$^{3+}$ ions do not replace Si$^{4+}$. I.r. spectra reveal strong OH absorption at *ca.* 2.9 $\mu$m,[59] and natural grossulars with a composition between Ca$_3$Al$_2$Si$_3$O$_{12}$ and 3CaO,Al$_2$O$_3$,2SiO$_2$,2H$_2$O are known.[34] Crystals from close to the classical grossular composition to 3CaO,Al$_2$O$_3$,6H$_2$O have been synthesized:[60] in fact it is difficult to grow grossular under anhydrous conditions.[61] Clearly, 4H$^+$ ions replace Si$^{4+}$, thus accounting for the broad grossular Mössbauer and optical absorptions. The 443 nm interstellar band is narrow (half-width 3 nm, 150 cm$^{-1}$) and there are no bands of comparable intensity within 10 nm (Figure 2), showing that all Fe$^{3+}$ ions in the grains have the same next-nearest neighbour environment. This eliminates Fe$^{3+}$-bearing silicates in which there is considerable replacement of Si$^{4+}$ by Fe$^{3+}$ or Al$^{3+}$ as a cause of the DIB's.

**D. Racah Parameters.**—The smaller separations of the Russell–Saunders states in complexed ions have been attributed to the expansion of the $3d$ electron clouds so as to encompass both cation and anion nuclei (the nephelauxetic effect).[62] The Racah $B$ and $C$ parameters described the effects of interelectronic repulsion. Jorgensen believes that the ratio ($\beta$) of the $B$ parameter of the complexed ion to the $B$ parameter of the free ion ($B_0 = 930$ cm$^{-1}$ for Fe$^{3+}$ and 785 cm$^{-1}$ for Mn$^{2+}$) is an indicator of degree of covalency. For Mn$^{2+}$ and Fe$^{3+}$ ions in silicates, $\beta$ values are *ca.* 0.85 and 0.55—0.7, respectively, showing that Fe$^{3+}$ bonds are more

[56] P. G. Manning, *Canad. Mineral.*, 1973, **12**, 215.
[57] R. G. Burns, *Canad. J. Spectroscopy*, 1972, **17**, 51.
[58] P. G. Manning, *Canad. Mineral.*, in the press.
[59] G. A. Slack and R. M. Chrenko, *J. Opt. Soc. Amer.*, 1971, **61**, 1325.
[60] E. P. Flint, H. F. McMurdie, and L. S Wells, *J. Res. Nat. Bur. Stand.*, 1941, **26**, 13.
[61] H. S. Yoder, *J. Geol.*, 1950, **58**, 221.
[62] C. K. Jorgensen, *Progr. Inorg. Chem.*, 1962, **4**, 73.

covalent than those of $Mn^{2+}$. Values of $B$ are calculated from the optical spectra using the expressions:

Energy separation of $^4A_1{}^4E(G)$ and $^6A_1(S)$ = $10B + 5C$, and
Energy separation of $^4E(D)$ and $^6A_1(S)$ = $17 + 5C$,

which are solutions of the Tanabe–Sugano equations.[63] Typical values of $B$ are listed in Table 4. For a series of natural garnets, $\beta$ values increase as anticipated with increasing ferric–oxygen distance.[32] Although trends in $B$ can be rationalized for a group of isostructural minerals, $B$-values are more useful in checking band assignments in ferric spectra and for predicting the energies of transitions to higher levels. The DIB marking the $^4E(D)$ level has not been identified, but a diffuse feature has been observed at 27 200 cm$^{-1}$ (368 nm).[26] Because the $^4A_1{}^4E(G)$ level is at 22 600 cm$^{-1}$ (443 nm), $B$ = 657 cm$^{-1}$ and $C$ = 3205 cm$^{-1}$. From the supernova spectra,[32] the $^4E(D)$ level is at 26 300 cm$^{-1}$ (380 nm), from which B = 530 and $C$ = 3460 cm$^{-1}$. A search by astronomers for the $^4E(D)$ band is desirable. Additionally, the third field-independent transition $^6A_1 \rightarrow {}^4A_2(F)$ in ferric ions is anticipated to occur at $22B + 7C$ or *ca.* 36 000 cm$^{-1}$ (278 nm):[64] a diffuse feature at this energy has not been confirmed.

**E. Broad Interstellar Absorption at *ca.* 625 nm (16 000 cm$^{-1}$).**—The presence of two broad features (half-width 2000 cm$^{-1}$) on the interstellar extinction curve at *ca.* 625 and *ca.* 417 nm was alluded to in Section 2A. Intervalence charge-transfer processes contribute in large measure to the colours and pleochroism of materials, *e.g.* Prussian Blue[65] and biotite mica.[66] Electron-hopping processes are prominent in materials in which transition-metal ions in different valence states are located at the centres of adjacent edge-sharing octahedra. In this structural arrangement, internuclear separations are often <0.3 nm and non-bonding $t_{2g}$ orbitals overlap *via* oxygen $2p\pi$ orbitals. The common processes in minerals are $Fe^{2+} \rightarrow Fe^{3+}$ and $Fe^{2+} \rightarrow Ti^{4+}$.[67] The former process is observed in the 730—550 nm region of the spectrum and the latter in the 475—415 nm region (except for $Fe^{2+}$ and $Ti^{4+}$ ions in $Al_2O_3$, corundum,[68] in which a polarized band is observed at *ca.* 670 nm). Respective $\epsilon$-values for bands marking the two processes are *ca.* 150 and >10$^4$ l mol$^{-1}$ cm$^{-1}$. Ion-pair concentrations are calculated assuming a random distribution of cations over a given site: this requires a collation of chemical analyses and crystal-chemical arguments (particularly for $Ti^{4+}$ distributions) and, additionally for Fe, Mössbauer data. Electron-hopping occurs when the vibration direction ($E$) of the electric vector of polarized light is parallel to the metal–metal axis. Micas absorb strongly when $E$ is in the plane of the cleavage flake, which plane contains transition-metal ions in adjacent edge-sharing

[63] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, 1954, **9**, 753.
[64] L. S. Heidt, G. F. Koster, and A. M. Johnson, *J. Amer Chem Soc.*, 1958, **80**, 6471.
[65] M. B. Robin, *Inorg. Chem.*, 1962, **1**, 337.
[66] G. H. Faye, *Canad. Mineral.*, 1968, **9**, 403; D. W. Robbins and R. G. J. Strens, *Chem. Comm.*, 1968, 508.
[67] G. H. Faye, P. G. Manning, J. Gosselin, and R. J. Tremblay, *Canad. Mineral.*, 1974, **12**, 370; N. S. Hush, *Progr. Inorg. Chem.*, 1967, **8**, 391.
[68] M. G. Townsend, *Solid State Comm.*, 1968, **6**, 81.

octahedra.[66] The intensity of the polarized band at 730 nm in biotite spectra is proportional to the product of the $Fe^{2+}$ and $Fe^{3+}$ concentrations. The band half-width is *ca.* 150 nm (3000 cm$^{-1}$).

In magnetite, the 16-fold octahedral positions are occupied by equal concentrations of ferrous and ferric ions, and the four-fold tetrahedral positions are occupied by ferric.[69] Each ferrous ion shares four octahedral edges with adjacent octahedrally bonded ferric ions. The $Fe^{2+}$ concentration is 22.5 mol l$^{-1}$; hence the concentration of $Fe^{2+}$–$Fe^{3+}$ ion pairs is 90 mol l$^{-1}$. Calculating as above, the average density of $Fe_3O_4$ in interstellar space is $0.5 \times 10^{-26}$ g cm$^{-3}$ and that of Fe $0.4 \times 10^{-26}$ g cm$^{-3}$. This suggests that an oxide such as $Fe_3O_4$, with ferric and ferrous ions in adjacent edge-sharing octahedra, could account for the 625 nm interstellar band. The broad absorption at *ca.* 417 nm, in the region of the corner, could then be assigned to $Fe^{2+} \rightarrow Ti^{4+}$. Titanium, as $Ti^{4+}$ on octahedral positions, is a common impurity in magnetites, and an equivalent number of octahedral ions are reduced to ferrous. The relatively low cosmic abundance of Ti is counteracted to a degree by the large $\epsilon$-value of the $Fe^{2+} \rightarrow Ti^{4+}$ process compared with that for $Fe^{2+} \rightarrow Fe^{3+}$.

**F. Grain Sizes and Temperatures.**—By placing a polarizing crystal in the focal plane of the telescope the degree of polarization of starlight can be measured. If the difference in magnitudes between maximum and minimum intensities as the polarizer is rotated is denoted $\Delta m_p$, and if $\Delta m$ is the mean of the magnitudes at maximum and minimu, then $\Delta m_p/\Delta m$ rarely exceeds 5%. Starlight is more strongly absorbed when the vibration direction of the electric vector is perpendicular to the galactic plane. The polarization is caused by the anisotropy (or dichroism) of interstellar grains promoting systematic alignment of the grains in space. Grains containing super-paramagnetic impurities, for example small particles of $Fe_3O_4$ or $Fe_2O_3$, would be aligned in the weak galactic magnetic field.[70] Recent measurements suggest that the DIB's are polarized to the same degree as the continuum.[71,27] Anomalous polarization across the 443 nm band would confirm its granular origin. It is possible, therefore, that there is one population of polarizing grains without diffuse features and a second population of weakly polarizing Fe-bearing grains. These results further suggest that the grains causing the diffuse bands are probably $\ll 10^4$ nm across.[72]

Duley has pointed out that the symmetry and the strength of the crystal-field at the surface sites will be different from at sites in the bulk.[72] This would induce shifts of bands in the crystal-field spectra. In most laboratory experiments the number of ions in surface sites is small compared with the total numbers of ions. Surface stresses are compressive, and using the pressure-induced shift data compiled by Drickamer,[73] Duley calculated that for 100 Å grains of $Ni^{2+}$:MgO

[69] E. J. W. Verwey and E. L. Heilmann, *J. Chem. Phys.*, 1947, **15**, 174.
[70] R. V. Jones and L. Spitzer, *Astrophys. J.*, 1967, **147**, 943.
[71] M. F. M'Hearn, *Astron. J.*, 1972, **77**, 302.
[72] W. W. Duley, *Astrophys. Space Sci.*, 1975, **36**, 345.
[73] H. G. Drickamer, *Solid State Phys.*, 1965, **17**, 1.

the 408 nm transition is shifted to shorter wavelengths by *ca.* 3 nm (200 cm$^{-1}$). It is anticipated, therefore, that the spectra of small grains will comprise a sharp band marking transitions in bulk ions and a broad band corresponding to transitions in ions in a range of surface sites. Significantly, it has been pointed out that several DIB's appear to occur in pairs with reasonable shifts.[72,23]

A perfectly black body in space attains a temperature of 3 K, but grains are warmer than this because their small size makes them poor emitters in the far i.r. Duley has shown that the temperatures of small grains (*ca.* 10$^3$ nm) are expected to be highly irregular functions of time because of large fluctuations produced by absorbed photons.[74] His calculations suggest that grains spend a significant amount of time (*ca.* 10 %) at temperatures exceeding the time-averaged temperature (5—20 K). A 10 nm particle of $Fe_2O_3$ will be raised to *ca.* 50 K on absorption of a 10 eV photon. Grains in dense clouds would accrete mantles of solid CO at time-averaged temperatures < 20 K. No observational evidence has been reported so far for CO-coated grains, suggesting that most grains do not possess mantles.

## 4 Concluding Remarks

A high degree of subjectivity in the choice of scattering and absorbing compounds is inherent in all approaches to the interpretation of stellar spectra. Because the interstellar extinction curve shows only a few broad inflexions, a unique solution will prove difficult. Even if significant quantities of silicate and graphite grains do exist in the interstellar medium—and elemental abundances suggest that they could—there is no guarantee the grains are crystalline rather than amorphous. Amorphous carbon will not absorb at 217.5 nm but amorphous silicate will still absorb at *ca.* 10 000 nm. Neither is it possible currently to distinguish between amorphous and crystalline iron oxides as the cause of the diffuse bands, but the small half-widths do suggest considerable short-range order.

The grains may comprise a core, of, say, graphite, silicate or iron oxide and a mantle of solid $H_2$, CO, *etc.* Do the diffuse bands originate in transitions within the core, in the mantle or at the core–mantle interface? Duley's calculations on grain temperatures suggest that the core origin is correct.

Two questions prompt areas for future research. To what extent are the crystal-field spectra of very small particles, say of radii 10 nm, different from the spectra of μm-size particles? Secondly, do the numerous diffuse bands of half-width <1 nm represent zero-phonon transitions in transition-metal bearing solids?

The crystal-field approach offers a reasonable explanation for the origin of the broader and more prominent diffuse bands, especially in view of the cosmic abundance of Fe and the field-independent character of some of the ferric transitions. Wavelength coincidences are not perfect, but this is not surprising because ferric ion crystal-field bands, though field-independent, do shift in

[74] W. W Duley, *Astrophys Space Sci.*, 1973, **23**, 43

wavelength from one mineral to another. Radiation damage of the interstellar grains may be extensive. Assignments for several of the sharp diffuse bands would be particularly desirable. The very broad absorptions on the extinction curve are strong contenders for a solid-state origin.