$$\sigma_{zz} = \tfrac{1}{3} \mathrm{Tr}\,\boldsymbol{\sigma} + \tfrac{1}{3}(3\cos^2\theta_\parallel - 1)(\sigma_\parallel - \sigma_\perp) \qquad (6\text{-}29)$$

where $\mathrm{Tr}\,\boldsymbol{\sigma}$ is now $(\sigma_\parallel + 2\sigma_\perp)$, and $(\sigma_\parallel - \sigma_\perp)$ is commonly referred to as the value of the shielding anisotropy. The convention $|\sigma_{33} - \tfrac{1}{3}\mathrm{Tr}\,\boldsymbol{\sigma}| \geqslant |\sigma_{11} - \tfrac{1}{3}\mathrm{Tr}\,\boldsymbol{\sigma}| \geqslant |\sigma_{22} - \tfrac{1}{3}\mathrm{Tr}\,\boldsymbol{\sigma}|$ is usually used, so that the order may be $\sigma_{11} \leqslant \sigma_{22} < \sigma_{33}$ or $\sigma_{11} \geqslant \sigma_{22} > \sigma_{33}$.

The consequence of these facts is that for a single crystal containing nuclei which are all in translationally equivalent positions, the NMR spectrum will consist of only one line whose frequency varies with the orientation of the crystal in B_0. For a microcrystalline powder sample, on the other hand, the distribution of nuclear orientations results in absorption over a *range* of frequencies, giving a *powder pattern*. A schematic powder pattern for the case of axial symmetry is shown in Fig. 6-9(b), and a practical example is illustrated in Fig. 6-10(a). The extrema give immediate measures of $\sigma_\parallel$ and $\sigma_\perp$. The corresponding general case is depicted in Fig. 6-9(c). Thus values of the principal components of shielding tensors are available from solid-state NMR spectra provided (a) dipolar interactions can be removed, and (b) overlapping between powder patterns for non-equivalent sites is not serious. Carbon-13 shielding anisotropies typically range upwards to 438 ppm[6] (see Section 8-16).

6-7 High-resolution NMR of dilute spins

In order to achieve high-resolution spectra of nuclei like ^{13}C in solids, three problems have to be overcome, viz:
(a) Broadening due to heteronuclear dipolar interactions (typically (^{13}C, ^{1}H)).
(b) Low sensitivity due to long ^{13}C spin–lattice relaxation times.
(c) Broadening due to shielding anisotropy.
In the mid-1970s it was realized[7] that a combination of three previously-known techniques could overcome the difficulties.

The effects of heteronuclear dipolar interactions can be eliminated from the spectra by the double-resonance procedure of decoupling the protons using an appropriate second r.f. exactly as for the electron-coupled scalar interactions discussed in Sections 1-11, 1-18 and 4-8. However, because of the strength of dipolar coupling very high decoupling powers (ca. 100 watts) are required, and for a long time this gave technical problems. The technique is known as high-power or dipolar decoupling. The latter term is, however, somewhat misleading, since scalar decoupling occurs at the same time.

Section 6-5 showed that problem (b) can be overcome by the cross-polarization procedure. The pulse sequence shown in Fig. 6-6 incorporates high-power decoupling while the ^{13}C FID is recorded, thus overcoming problem (a) simultaneously.

The form of the second term in Eqns 6-28 and 6-29 recalls the discussion of Section 6-2 and suggests the solution to problem (c), viz. magic-angle rotation. As noted in Section 6-2 the achievable rates of MAR are inadequate to eliminate dipolar interactions in general, but
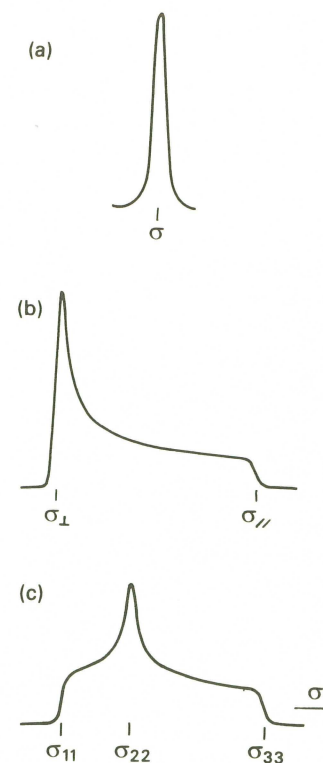

Fig. 6-9 Schematic powder patterns caused by shielding anisotropy for a site with (a) cubic symmetry, (b) axial symmetry, (c) lower symmetry.
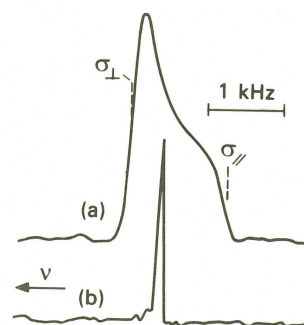

Fig. 6-10 Lead-207 spectra of solid lead nitrate, (a) static, and (b) with MAR. [Adapted, with permission, from D. J. Burton, R. K. Harris & L. H. Merwin, *J. Magn. Reson.*, **39**, 159–162 (1980), but with the direction of the frequency axis corrected.]

broadening arising from ^{13}C shielding anisotropy is substantially lower than (^{13}C, ^{1}H) dipolar broadening, and so requires relatively modest MAR speeds (e.g. ca. 3 kHz if $B_0 = 2\cdot35$ T), which are achievable. If rates lower than the shielding anistropy (expressed in Hz) are used, then satellite resonances called *spinning sidebands* are seen. This implies that the difficulties in obtaining good high-resolution spectra increase as the operating field B_0 increases. Happily MAR eliminates the small broadening due to dipolar interactions between the dilute spins themselves. Thus, in favourable cases, spectra with linewidths of only a few Hz may be obtained.

Figure 6-10 shows the improvement in resolution obtained by the final-stage MAR process in the case of lead nitrate, and Fig. 6-11 shows the effect of both high-power decoupling and MAR for calcium acetate. Although the aim of the techniques discussed in this section is to produce NMR spectra of solids which are comparable in resolution to those of liquids, it is not to be supposed that identical spectra will be obtained. Indeed the principal interest will often lie in the differences. Two such situations will be mentioned here. Firstly, crystallographic effects sometimes give rise to splittings of lines. In order for a particular type of carbon to yield a single line, all those carbons must be related by symmetry *in the crystal*. It is, however, not uncommon for such carbons to occupy crystallographically non-equivalent sites, in which case they will give rise to two (or more) resonances. Such non-equivalence may be intramolecular or intermolecular, and an example is given in Fig. 6-11(d). The second situation to be mentioned is, in a sense, similar: for non-crystalline (amorphous) solids, particularly many polymers, there is a *dispersion* of environments for a given carbon. This will lead to line broadening rather than line-splitting. Typical ^{13}C linewidths for glassy polymers are ca. 2 ppm from this cause. Figure 6-12 shows how widths vary for a cross-linked epoxide.

Obviously chemical shifts for solids will differ to some extent from those for solutions of the same materials. This is clearly shown by cases with additional splittings (see Figs. 6-11, 6-13 and 6-16). Variations can sometimes be attributed to general 'medium' effects, i.e. changes in environment such as also occur for solutions. In other cases conformational changes may be involved, or tautomeric differences. One particularly important type of variation is provided by cases of polymorphism, of importance in the pharmaceutical and polymer industries. Figure 6-13 illustrates a case where the solid-state ^{13}C spectra of two polymorphs are discernibly different. Such differences can be exploited for analytical purposes on the one hand and, if crystal structures are known, for the understanding of factors affecting chemical shifts on the other. The spectra of both polymorphs shown in Fig. 6-13 indicate the non-equivalence of all three of the citrate carboxyl carbons in the solid state; these carbons give rise to the three peaks at highest frequency in each case.

High-resolution carbon-13 NMR for solids is now well-established,