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Analysis of Wide Line NMR Powder Patterns Perturbed by Second-order Nuclear Quadrupole Interactions. Investigation of the Three-fold Symmetry of the BO_3-Group in Vitreous and Crystalline Boron Oxide

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Fourier transforms are shown to be useful in the analysis of powder patterns perturbed by second-order nuclear quadrupole interactions, the frequency dependence of the transforms being used to test the validity of the simplifying conditions introduced in order to facilitate the analysis. The method of analysis is applied to the spectra of vitreous and crystalline B_2O_3, and it is shown that these spectra have a shape which indicates a very nearly three-fold symmetrical configuration of the BO_3-group in these substances.

In an earlier NMR study it was concluded that the BO_3-group has a planar structure in vitreous and crystalline B_2O_3.[1] The conclusion was drawn from a comparison between the values of the quadrupole coupling constants of these compounds and a number of crystalline substances of known structure. It was further shown that the shape of the spectra are in rather close agreement with three-fold symmetry of the group. This latter fact formed a fundamental link in the deduction of a planar structure. For a symmetric group the asymmetry parameter η is equal to zero and the value of the quadrupole coupling constant, eqQ, could easily be determined from the peak-to-peak separation between the high and low field component lines of the spectrum. In order to establish the symmetry and thus the planar structure of the BO_3-group, a more detailed analysis of the line shape was attempted. The investigation has also value in that it should help us to form an opinion as to the degree of short range order in the vitreous form of B_2O_3, with regard to the bond angles at the boron atoms.

METHOD OF ANALYSIS

For the NMR spectrum to be observable the electric quadrupole interaction energy has to be small compared with the Zeeman interaction energy. In calculating the quadrupole effects on the magnetic resonance spectra, the quadrupole interaction are then treated as perturbations of the purely magnetic interactions. The quadrupole dependent frequency shifts are expressed, in the theoretical treatment, as a power series of the parameter eqQ/ν_0, where eqQ denotes the quadrupole coupling constant and ν_0 the frequency of the unshifted resonance. For single crystals, the quadrupole interaction results in a splitting of the spectrum into a number of component lines representing the allowed transitions between different sets of magnetic quantum numbers. The random orientation in a powdered sample gives rise to a continuous distribution of frequency shifts, usually resulting in a broad spectrum of low signal strength. Depending on the relative magnitude of the quadrupole interaction two discrete cases, easily distinguishable, may arise. First order powder patterns are obtained when the quadrupole interaction is so weak that the frequency shifts can be expressed by the first term in the power series. For nuclei of half-integral spin, the central component line, representing the transitions $m=-\frac{1}{2}$ to $m=+\frac{1}{2}$, which is unshifted to a first order approximation, is still observable for a comparatively large interaction, which means that the frequency shifts may be expressed by the first and second terms, only, of the series expansion. The resulting second order powder patterns are frequently observed, and for the analysis of this type of spectrum the following method is suggested. If the satellites do not contribute to the observed spectrum the line shape function generated by the quadrupole interaction can be written as

$$Q(\xi) = \nu q(\nu\xi) \tag{1}$$

where ξ denotes the magnetic field coordinate measured from the position of the unperturbed resonance, and ν gives the frequency of the h.f. field. The equation simply expresses the fact that the frequency shifts are inversely proportional to ν. Besides the quadrupole interaction, the pure dipole interaction must be taken into consideration. In most treatments presented, the dipolar broadening is superimposed on the quadrupole broadening by use of a folding integral containing the two appropriate broadening functions. In this treatment a mutual independence of the two broadening mechanisms is assumed, which, in this case, requires the dipolar broadening function to be independent of the orientation of the external magnetic field in the crystal lattice. This is indeed an approximation, which we may adopt in order to make the problem feasible for calculation. Denoting the line shape yielded by the dipolar coupling as $P(x)$, the line shape function may be calculated as

$$f(x) = K(\nu) \int_{\xi_1}^{\xi_2} P(x-\xi)\ \nu\ q(\xi\nu)\ d\xi \tag{2}$$

where $K(\nu)$ denotes the frequency dependent sensitivity of the spectrograph. By performing the analysis in Fourier transform notation, the treatment of the folding integral is greatly simplified.[2]

We calculate the transforms with the position of the unshifted signal as origin, and divide all calculated quantities by M_0, the area under the absorption line, in order to eliminate $K(\nu)$. In many earlier applications of the folding integral in the calculation of NMR line shapes, the dipolar broadening function has been presumed to be Gaussian. In order to facilitate a simple method of analysis when applying the Fourier transforms we need only to assume that this function is symmetrical. The theory shows that the pure dipole broadening gives rise to symmetrical spectra. Due to the partial quenching of the flip-flop terms of the dipolar Hamiltonian the component lines of a resolved spectrum, split, for example, by a quadrupole interaction, will not, however, be symmetrical in cases where a large anisotropy of the dipolar interaction occurs. The dipolar broadening of the central transition seems, however, to yield shape functions of a comparatively low degree of asymmetry, as is demonstrated, for example, by the ^{27}Al resonance from an Al_2O_3 single crystal.[3] The heavily anisotropic interaction of the crystal studied leads to pronounced asymmetrical shape functions for the satellites but to a symmetrical central line shape. From the positions of the completely resolved component lines of the spectrum, the presence of second order interaction terms of the quadrupole coupling may be established. The symmetrical shape of the resolved component line assigned to three-coordinated boron is furthermore evident from the NMR spectra reproduced in the literature of single crystal investigations.[4,5]

The transforms are obtained as

$$F_m(u,\nu) = \frac{1}{M_0(\nu)} \int_{-\infty}^{+\infty} f_\nu(x) \cos ux \, dx = S(u) \int_{y_1}^{y_2} q(y) \cos u(y/\nu) dy$$

$$G_m(u,\nu) = \frac{1}{M_0(\nu)} \int_{-\infty}^{+\infty} f_\nu(x) \sin ux \, dx = S(u) \int_{y_1}^{y_2} q(y) \sin u(y/\nu) dy$$

$$S(u) = P(\xi) \cos u\xi \, d\xi$$

where $y = \nu\xi$.

As the shape function $q(\nu\xi)$, yielded by the second order quadrupole interaction, comprises a symmetrical and an unsymmetrical part, we can construct the quotient F_m/G_m and hereby eliminate the effect of the dipolar broadening. The F_m/G_m quotient is thus well suited for the adaptation of eqQ and η to the experimental results. The conditions necessary for the elimination of the dipolar broadening effect in the quotient can furthermore be tested from the frequency dependence of the quotient. Starting from the folding integral and following the development given, it is easily shown that a quotient of the form $F_m(au,av)/G_m(au,av)$ is independent of the parameter a.

The most important condition to be tested by the frequency dependence concerns the mutual independence of the distributions P and q. As is pointed out above, this condition is necessary if the line shape is to be written as the convolution of P and q. If, on the other hand, the quotient is significantly dependent on a, this may be the result of a number of other circumstances. Such a dependence will occur if higher order terms also have to be included in the power series expansion of the quadrupole perturbed frequency shift, or if the satellites contribute to the observable part of the spectrum, to some degree. It may also be due to an asymmetrical shape of the dipolar broadening function as is indicated above.

In the actual applications, the calculation of the quotient F_m/G_m proved, however, to be somewhat inadequate. Since the unsymmetrical part of the distribution, q, is comparatively small, large errors arise in G_m when calculated from the spectra of the B_2O_3 samples, which exhibit a rather low signal-to-noise ratio. In this case, since the dipolar broadening function is narrow compared with the quadrupole broadening function, we may instead make use of the F_m transform only, which can be calculated with better accuracy. In a limited interval of comparatively small values of u, within which the transform $S(u)$ of the narrow dipolar distribution could be regarded as being constant and equal to $S(0)$, the variation of $F_m(u,\nu)$ with u depends upon the transform of q. If the difference in line width between the two distributions is sufficiently large, we may obtain enough information about the distribution, q, from this limited interval of u to determine the unknown parameters of the distribution, eqQ and η. From the frequency dependence of $F_m(u,\nu)$ it is possible to test whether or not the conditions necessary for the analysis are fulfilled. Within the interval of u in which $S(u)$ could be regarded as being constant, $F_m(au, a\nu)$ is, namely, independent of a if these conditions are fulfilled. For this type of analysis we do not need to assume a mutual independence of the two broadening functions. The only requirement is that the broadest component of the dipolar broadening function is sufficiently narrow compared with the quadrupole broadening function to facilitate the analysis. This means, in the application of prime interest here, that the analysis holds true even in cases where the dipolar broadening depends on the orientation of the magnetic field in the substance. Some asymmetry of the dipolar broadening function can furthermore be accepted since the sine transform of the distribution, P, is very small compared with the cosine transform $S(u)$ in the interval of u in which $S(u)$ can be regarded as being constant.

The methods outlined for the analysis of NMR spectra may find use in many other applications of spin resonance spectroscopy. The usefulness of the methods in treating spectra of powdered metal samples exhibiting anisotropic Knight shifts is obvious. The shape function yielded by the anisotropic Knight shift of the powdered sample may be written

$$Q_\nu(\xi) = (1/\nu)q(\xi/\nu)$$

since the size of these shifts are proportional to the frequency ν of the h.f. field.

APPLICATION TO THE SPECTRA OF VITREOUS AND CRYSTALLINE BORON OXIDE

Spectra of the samples were recorded at 10.000 and 16.000 Mc/s. A Varian-4250 wide line spectrometer was used, the frequency of the h.f. field being stabilized by the frequency from a digital counter. The magnetic scan was calibrated using the usual sideband technique and a sample of solid $NaBH_4$ which gave a narrow signal of an intensity sufficient to allow the observation of the sidebands. The total scan of 100 gauss was reproducible to within 1 %. The transforms were calculated on a digital computer, each spectrum being represented by one hundred equally spaced measurements. Proper corrections for modulation broadening were also introduced into the computer.[6] All transforms were calculated with the position of the unshifted signal as origin, which was determined from the site of the $NaBH_4$ resonance. Transforms, F_m (u, ν = 16.0 Mc/s) of the broad signal assigned to three-fold coordinated boron in vitreous and crystalline boron oxide and a potassium borate glass containing 30 mole % K_2O are shown in Fig. 1.

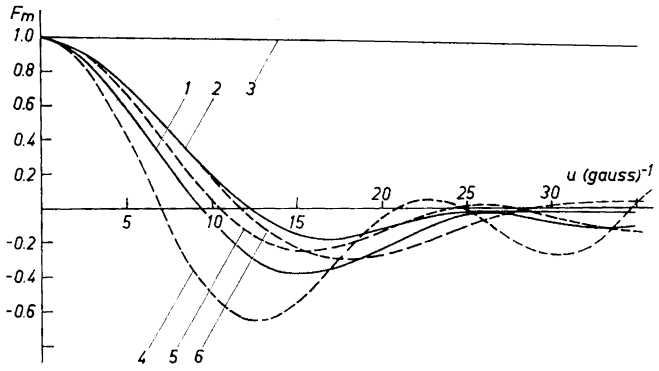

Fig. 1. Normalized cosine-transforms of spectra registered at 16.00 Mc/s.

1. Vitreous and crystalline boron oxide.
2. Potassium borate glass containing 30 mole % K_2O.
3. The transform of the dipolar broadening function of assumed Gaussian shape and an estimated rms width of 1.3 kc/s.
4, 5, 6. Calculated transforms of the pure second order patterns

for $\eta = 0.0$ $eqQ = 2.76$ Mc/s,
$\eta = 0.1$ $eqQ = 2.65$ Mc/s and,
$\eta = 0.2$ $eqQ = 2.50$ Mc/s, respectively.

The transform, F_m ($10u/16$, ν = 10.0 Mc/s) of these spectra coincide perfectly with F_m (u, ν = 16.0 Mc/s) for values of u up to 0.25 (gauss)$^{-1}$ and, as the transforms exhibit a rapid variation with u in this interval, the conditions for studying the shape function generated by the quadrupole interaction are most satisfactory. The cosine transform of the dipolar broadening

function, assumed to be Gaussian and of an rms width of 1.3 kc/s, as previously estimated for the B_2O_3 system, also exhibits a very slow variation with u in this interval, as shown in the figure. The restriction as to the use of the cosine transforms, only, is then fully justified. For the purposes of comparison, the transforms of q have been calculated for $\eta = 0.1$ and 0.2 using the numerical data for the previously computed q distributions.[7] Values of eqQ have been chosen so as to give peak-to-peak separations corresponding to those observed in the appropriate spectra. The transforms of the spectra of vitreous and crystalline B_2O_3, which are completely identical, display a functional dependence which lies somewhere between the curves of $\eta = 0.0$ and 0.1. A value of η around 0.04 seems to be a reasonable estimate, and as this value is smaller than the values normally found in the borate structures, a configuration of the BO_3-group with symmetry close to three-fold seems likely. The transforms of the sample of borate glass have a shape which indicates a value of η larger, rather than smaller, than 0.1. The value of the quadrupole coupling constant which could be estimated in this case, is also in close agreement with those determined from single crystal investigations.

The examples studied clearly demonstrate the usefulness of the method of analysis. By using transform notation we can neglect the effect of dipolar broadening and adapt the quadrupole yielded shape function to the experimental results in an interval of small values of u. This is valid when the dipolar broadening is narrow compared with the quadrupole broadening function. As the spectra studied show, even in such cases, the dipolar broadening causes a considerable smoothening out of the structure of the quadrupole function, so that this function cannot be studied in detail from the observed line shape function. We have not attempted to go further into details for estimating the accuracy obtained in such an analysis in which the shape of a spectral line is repesented in Fourier transform notation. Our aim is to demonstrate the usefulness of the transform notation, which permits a very convenient handling of the problem and facilitates a test of the validity of all simplifying assumptions introduced.

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