With an rf field applied in the x- or y-direction of the rotating frame respectively, the “external” Hamiltonian can be written as
\[ H_{\text{ext}} = -\omega_1(t) I_{x,y} \] (4)
with
\[ \omega_1(t) = \gamma H_1(t). \]

Leading to the propagator
\[ L_1(t) = e^{i\beta(t) I_{x,y}} \] (5)
with
\[ \beta(t) = \int_0^t dt' \omega_1(t'). \]

Since \( L_1(t) \) operates only on the spin dependent part of the interaction Hamiltonian in Eq. (3 c), \( H_{\text{int}} \) is conveniently written as a product of tensor operators \(^7\)
\[ H_{\text{int}} = \sum_{M=-J}^{+J} (-1)^M A_j M T_{JM} \] (6)
where the different interactions can be distinguished by \( j \) (\( j = 1 \) magnetic shielding, \( j = 2 \) dipolar and quadrupolar interaction).

The spin dependent part \( T_{JM} \) is modulated according to Eqs. (3 c), (5) and leads in the rotating frame to
\[ \tilde{H}(t) \propto \tilde{T}_{J0} \] (7)
where
\[ \tilde{T}_{J0} = [L_1^{-1}(t) T_{JM} L_1(t)]_{M=0} \] (8)
which can be expressed as
\[ \tilde{T}_{J0} = \sum_{M=-J}^{+J} T_{JM} D_{M0}^{(J)}(\alpha, \beta, 0), \] (9)
where the Wigner matrices \(^7\)
\[ D_{M0}^{(J)}(a, \beta, 0) \] can be written as
\[ D_{M0}^{(J)}(a, \beta, 0) = e^{-iM2} D_{M0}^{(J)}(\beta) \] (10)
and where \( a \) determines the rf field direction.

Using Eqs. (9), (10) we obtain:
(i) y-irradiation \((a = 0)\)
\[ \tilde{T}_{10} = T_{10} \cos \beta + (T_{1-1} - T_{1+1}) \frac{1}{\sqrt{2}} \sin \beta, \] (11 a)
\[ T_{20} = T_{20} \frac{1}{2} (3 \cos^2 \beta - 1) \]
\[ + (T_{2-1} - T_{2+1}) \sqrt{3} \sin \beta \cos \beta, \] (11 b)
\[ + (T_{2+2} + T_{2-2}) \sqrt{3} \sin^2 \beta, \]
(ii) x-irradiation \((a = -\pi/2)\)
The terms with \( M = \pm 1 \) in Eq. (11) are multiplied by \( \pm i \), whereas the terms with \( M = \pm 2 \) are multiplied by \(-1\). The average Hamiltonian during rf irradiation is immediately obtained as
\[ \tilde{T}_{J0}(\beta_1) = \frac{1}{\beta_1} \int_0^{\beta_1} d\beta \tilde{T}_{J0} \] (12)
where
\[ \beta_1 = \int_0^{t_p} dt \omega_1(t). \]

Fig. 1. Timing of the four-pulse sequence, where \( t_p \) is the pulse width, and with the cycle times \( t_s \) of the subcycle and \( t_c \) of the full cycle. There are two “windows” of duration \( \tau_1 \) and \( \tau_2 \) in each subcycle. \( y \) and \( x \) denote the direction of rf irradiation in the rotating frame.

The way in which the average Hamiltonian over a cycle of rf pulses can be calculated will be demonstrated in the case of the subcycle of the four-pulse experiment (see Fig. 1), which is essentially a phase alternated pulse experiment with cycle time
\[ t_s = 2 t_p + \tau_1 + \tau_2. \]
If we use the abbreviation \( k = \tau_1/\tau_2 \) and introduce the duty factor \( \delta = 2 t_p/t_s \) we obtain the average Hamiltonian over the cycle time \( t_s \) as
\[ \langle \tilde{T}_{J0} \rangle_{ts} = \delta T_{J0}(\beta_1) + \frac{k(1-\delta)}{1+k} \tilde{T}_{J0}(\beta_2) + \frac{(1-\delta)}{1+k} \tilde{T}_{J0}(0) \] (13)
which can be written in compact form as
\[ \langle \tilde{T}_{J0} \rangle_{ts} = \sum_{M=-J}^{+J} T_{JM} D_{M0}^{(J)}(\alpha, \beta, 0) \] (14)
where the coefficients \( D_{M0}^{(J)}(\alpha, \beta, 0) \) can be derived by using Eqs. (9) – (13). By using the abbreviations
\[ D_0 = \overline{D_{00}^{(1)}(0, \beta, 0),} \]
\[ D_1 = \overline{D_{10}^{(1)}(0, \beta, 0),} = \overline{D_{11}^{(2)}(0, \beta, 0),} \]
\[ D_2 = \overline{D_{20}^{(1)}(0, \beta, 0),} = \overline{D_{22}^{(2)}(0, \beta, 0),} \]
\[ D_0 = \overline{D_{00}^{(2)}(0, \beta, 0),} \]
\[ D_1 = \overline{D_{10}^{(2)}(0, \beta, 0),} \]
\[ C_0 = \overline{D_{00}^{(1)}(0, \beta, 0),} \]
\[ C_1 = \overline{D_{10}^{(1)}(0, \beta, 0),} = \overline{D_{11}^{(2)}(0, \beta, 0),} \] (15)
we obtain from Eqs. (9) – (15):
\[ D_0 = \frac{3}{2} \cos \beta_1 \left\{ \frac{k(1-\delta)}{1+k} \cos \beta_1 + \delta \sin \beta_1 \right\} \\
+ \frac{1}{2} \frac{(1-\delta)}{(1+k)} - \frac{3}{2} \beta_1, \quad (16 \text{a}) \]
\[ D_1 = V \frac{3}{2} \sin \beta_1 \left\{ \frac{\delta}{2} \sin \beta_1 + \frac{2}{1+k} \frac{k(1-\delta)}{1+k} \cos \beta_1 \right\}, \quad (16 \text{b}) \]
\[ D_2 = V \frac{3}{2} \sin \beta_1 \left\{ \frac{k(1-\delta)}{1+k} \sin \beta_1 - \frac{2}{1+k} \left( \frac{1}{2} \frac{k(1-\delta)}{2} \cos \beta_1 + \delta/2 \right) \right\}, \quad (16 \text{c}) \]
\[ C_0 = \delta \sin \beta_1 + \frac{k(1-\delta)}{2} \cos \beta_1 + \frac{(1-\delta)}{(1+k)} \right\}, \quad (16 \text{d}) \]
\[ C_1 = \frac{\delta}{2} \sin \beta_1 \left\{ \frac{1}{1+k} + \frac{k(1-\delta)}{1+k} \sin \beta_1 \right\}. \quad (16 \text{e}) \]

The coefficients corresponding to irradiation in \( x \)-direction (\( \alpha = -90^\circ \)) are easily obtained by multiplying \( D_1^\text{\(y\)} \) by \( \pm i \) in the case of \( M = \pm 1 \) and by \( -1 \) in the case of \( M = \pm 2 \).

Thus scaling of second rank tensor interaction (e.g. dipolar interaction) and first rank tensor interaction (e.g. magnetic shielding) in phase alternated pulsed nmr experiments can be easily calculated by combining Eqs. (14), (15), (16). From Eq. (16c) it follows that \( D_2 \) never can be made to vanish, besides trivial cases like \( \beta_1 = 0 \), i.e. the dipole interaction cannot be cancelled in a phase alternated experiment, where rf irradiation takes place only in one direction in the rotating frame. However, if another subcycle is added in which irradiation is performed orthogonal to the first one, \( D_2 \) is multiplied by \( -1 \) in the second subcycle and the total average vanishes, independent of the parameters \( \delta, k \) and \( \beta_1 \).

3. The Four-Pulse Experiment with Arbitrary Pulse Width

The timing of the four-pulse cycle with arbitrary pulse width is shown in Figure 1. The full cycle with the cycle time \( t_c \) consists of two subcycles with the cycle time \( t_c \) each, in which rf irradiation is performed in the \( y \)- and \( x \)-direction respectively.

The average Hamiltonian can be expressed as
\[ \langle \hat{T}_{20} \rangle_t = \frac{1}{2} \langle \hat{T}_{20} \rangle \rangle_t + \frac{1}{2} \langle \hat{T}_{20} \rangle \rangle_t \quad \text{(17)} \]

Since the term with \( M = \pm 2 \) in \( \langle \hat{T}_{20} \rangle_t \) vanishes independent of \( \delta, k \) and \( \beta_1 \) due to phase quadrature as mentioned above, the condition for line narrowing can be expressed as
\[ \langle \hat{T}_{20} \rangle_t = 0; \quad \text{i.e.} D_0 = D_1 = 0 \quad \text{(18)} \]

Thus we arrive at the question, for which set of \( (\delta, k, \beta_1) \) do \( D_0 \) and \( D_1 \) simultaneously vanish. From Eqs. (16 a, b) it can be shown, that this condition can be fulfilled only if
\[ \delta = \frac{2}{3} \frac{k-2}{k-1}. \quad (19) \]

This puts a restriction on the timing of the four-pulse sequence and it demands what we shall call the “ideal timing”. This “ideal timing” is nothing else, but the timing of the classical four-pulse cycle \( t_c \) in the \( \delta \) pulse approximation i.e. \( k = 2 \) if \( \delta = 0 \). If the pulse width is increased, the leading edge of the pulse is kept at the location of the \( \delta \) pulse in the cycle, and the pulse width is simply increased to the right, as shown in Figure 1. Under this condition the duty factor obeys Equation (19).

If the condition Eq. (19) is inserted in Eq. (16) we can write
\[ D_0 = \frac{3}{2} \cos \beta_1 \left\{ \frac{1}{2} \left( 2 - \frac{3}{2} \delta \right) \cos \beta_1 + \sin \beta_1 \right\}, \quad (20 \text{a}) \]
\[ D_1 = V \frac{3}{2} \sin \beta_1 \left\{ \frac{\sin \beta_1 + \frac{2}{1+k} \left( 2 - \frac{3}{2} \delta \right) \cos \beta_1 \right\}, \quad (20 \text{b}) \]
\[ D_2 = V \frac{3}{2} \sin \beta_1 \left\{ \frac{\sin \beta_1 + \frac{2}{1+k} \left( 2 - \frac{3}{2} \delta \right) \cos \beta_1 - \frac{2}{1+k} \cos \beta_1 + \delta/2 \right\}, \quad (20 \text{c}) \]
\[ C_0 = \frac{\delta}{2} \left\{ \frac{\sin \beta_1 + \frac{2}{1+k} \left( 2 - \frac{3}{2} \delta \right) \cos \beta_1 + \frac{1}{2} \left( 1 - \frac{3}{2} \delta \right) \right\}, \quad (20 \text{d}) \]
\[ C_1 = \frac{1}{2} \left\{ \frac{\sin \beta_1 + \frac{2}{1+k} \left( 2 - \frac{3}{2} \delta \right) \sin \beta_1 \right\}. \quad (20 \text{e}) \]

which yields the scaling factors in the case of the “ideal timing”.

\( D_0 \) and \( D_1 \) are plotted versus \( \beta_1 \) in Fig. 2 for different values of \( \delta \). It is interesting to compare this with far off-resonance effects. It can be seen, that \( D_0 \) and \( D_1 \) cross the zero line for the same value of \( \beta_1 \) as is demanded by the “line narrowing” condition Equation (18).

This condition \( (D_0 = D_1 = 0) \) leads to a dependence of the rotating angle \( \beta_1 \) on the duty factor \( \delta \).
Fig. 2. The remaining coefficients $D_0$ and $D_x$ in the average dipolar Hamiltonian in the four-pulse experiment with "ideal timing" according to Eqs. (20 a, b) are plotted versus $\beta$ for different values of the duty factor $\delta$. — Due to the "ideal timing" $D_0$ and $D_x$ cross the zero line always at the same value $\beta_{1}$, according to Eqs. (20 a) and (20 b) as follows:

$$\delta = \frac{\beta}{(1 - \tan \beta_{1} / \beta_{1})}.$$  \hspace{1cm} (21)

$\delta$ is plotted versus $\beta_{1}$ according to Eq. (21) in Figure 3. This figure can serve as a diagram for determining $\beta_{1}$ for a given value of $\delta$, i.e., there is for any given $\delta$ with $0 \leq \delta \leq 2/3$ a value $\beta_{1}$ for which line narrowing in solids can be achieved. For a small duty factor $\delta$, $\beta_{1}$ may be expressed as $\beta_{1} = \pi / 2 + \varepsilon$ where $\varepsilon$ is small. In this case Eq. (21) leads to

$$\delta = \frac{\pi}{2} \cdot \varepsilon,$$

which is the same result as Eq. (67) of Ref. 2.

The following procedure for adjusting the four-pulse experiment is suggested:
(i) set up the "ideal timing" according to Figure 1,
(ii) adjust the proper phases,
(iii) increase or decrease the rf power (not the pulse width!) in order to obtain a lengthened decay.

One must not change the pulse width, since in general this does not fulfill Equation (21).

There is an upper limit for $\delta$, which is given by the timing according to Equation (19). This upper limit is reached if $k = \infty$ $\delta_u = 2/3$ leading to the condition $^5$ [see Eq. (21)]

$$\tan \beta_u = - \beta_u$$

from which follows

$$\beta_u = 116^\circ 14'$$

The capability of achieving line narrowing in solids with such a four-pulse experiment in the ultimate pulse width limit is described elsewhere $^5$.

The scaling factor $S$ of the magnetic shielding in a four-pulse experiment and all other interactions which can be described by a first rank tensor operator can be expressed as

$$S = (C_0^2 + C_1^2)^{\beta_1},$$

where $C_0$ and $C_1$ are given by Eqs. (20 d, e) under the condition of Equation (21).

An analytical expression for $S$ as a function of $\beta_1$ can be obtained from Eqs. (20 d, e), (21), but is of not much interest here. Since the duty factor $\delta$ is an easily measurable quantity, we have calculated numerically $S$ as a function of $\delta$ by using Eq. (20 d, e) and Equation (21). $S$ is plotted versus $\delta$ in Figure 4.
The scaling factor $S$ for the magnetic shielding begins with $S = 1/\sqrt{3} = 0.577$ for $\delta = 0$ and decreases with increasing $\delta$, until the upper limit in pulse width is reached ($\delta_u = 2/3$), corresponding to $S = 0.565$. Nevertheless, the variation of the scaling factor $S$ with $\delta$ is seen to be very small.

The first order and all other higher correction Hamiltonians of odd order can be shown to vanish due to symmetry arguments.$^6$,$^9$

4. The Dipolar Echo produced by the Four-Pulse Sequence

A dipolar echo can be produced, using the four-pulse sequence$^{10,11}$, utilizing the fact that the average dipolar Hamiltonian can be made negative$^{10,11}$ if the parameter $k$ becomes greater than 2.

In the case of $\delta$ pulses, this can be shown easily by using the parameters $\delta = 0$ and $\beta_1 = 90^\circ$ in Equation (16). It follows from Eqs. (16 a, b) that under these conditions$^{10,11}$

$$D_0 = \frac{1}{2} \cdot \frac{2-k}{1+k}$$

whereas

$$D_1 = 0.$$  

Thus the average dipolar Hamiltonian becomes negative for $k > 2$ during a burst of four-pulse cycles of duration $t_B$. The motion of the spins governed by this negative average Hamiltonian redeveloples in time when the subsequent positive Hamiltonian $T_{20}$ is in effect. The echo condition can be written as

$$\frac{1}{2} \frac{k-2}{1+k} \cdot t_B + t - t_B = 0$$

or

$$t/t_B = \frac{3}{4} k/(1+k)$$

leading to the formation of an echo at time $t$, when the four-pulse burst is terminated at time $t_B$.$^{10}$

If a finite pulse width ($\delta \neq 0$) is used, the problem of forming a dipolar echo is more complicated, but can be solved by the means of Equation (16). $D_1$ can be made to vanish according to Equation (16 b) if

$$\delta = 1 \left( 1 - \frac{1+k}{2 k \beta_1} \tan \beta_1 \right).$$

In Eq. (26) $D_0$ is plotted versus $\beta_1$ for different parameters $k$, according to Equation (26).

If $\delta$ according to Eq. (26) is inserted in Eq. (16 a) we obtain

$$D_0 = \frac{1+\tan \beta_1 (k-2)/k \beta_1}{4 - 2 \tan \beta_1 (1+k)/k \beta_1}.$$  

In Fig. 5 the duty factor $\delta$ according to Eq. (26) for different values of $k$ is plotted versus the rotating angle $\beta_1$. This diagram serves in choosing the parameter sets ($\delta, k, \beta_1$) for obtaining a dipolar echo.

In Fig. 6 $D_0$ is plotted versus $\beta_1$ for the same parameters $k$ as in Figure 5. $D_0$ becomes negative only for $k > 2$ and $90^\circ \leq \beta_1 < 116^\circ 14'$. The echo condition Eq. (25) can be generalized to

$$D_0 t_B + t - t_B = 0$$

leading to

$$t/t_B = 1 - D_0$$

where $D_0$ is given by Eq. (27) with the parameters $k$ and $\beta_1$ obtained by Equation (26). From Eqs. (26) and (27) it follows, that for any duty factor $\delta$ with $0 \leq \delta < 2/3$ a dipolar echo can be obtained.

Acknowledgment

Valuable discussion and conversation with Professors O. KANERT and J. S. WAUGH is greatfully acknowledged.
Transporteigenschaften von Bi$_{70}$Sb$_{30}$

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(Z. Naturforsch. 27 a, 1639—1645 [1972]; eingegangen am 12. August 1972)

Transport Properties of Bi$_{70}$Sb$_{30}$

Crystals of the composition Bi$_{70}$Sb$_{30}$, undoped and doped with the donor Te and the acceptor Sn, were made by zone melting. Specimens were prepared with the long edges parallel to the bisectrix, the binary or the trigonal axis. Transport properties (electrical resistance, transverse magnetoresistance, Hall effect, thermoelectric power, longitudinal and transverse Nernst-Ettingshausen effect) were measured for specimens with different orientation and doping in the temperature range from 8 to 300 °K. Investigations of magnetic field dependence of some properties and of the anisotropy of magnetoresistance in a transverse field of different directions were made.

1. Einleitung


2. Probenherstellung und Meßverfahren


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