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Energy Levels of CaF_2:Gd^{3+} in a Cubic Crystal Field*

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The energy levels of Gd^{3+} in the cubic crystal field of CaF_2 are calculated using free-ion vectors computed with spin-other-orbit and spin-spin interactions included. The B_0^4 and B_0^6 coefficients are fitted to the experimental ${}^6P_{7/2}$ and ${}^6P_{5/2}$ splittings. Using only the 18 M_J components of the ${}^6P$ free-ion levels as a basis, values of $B_0^4 = -2270.79$ cm^{-1} and $B_0^6 = 730.65$ cm^{-1} are obtained. This calculation gives a mean error of 8 cm^{-1} between calculated and experimental levels. To improve the quality of the fit, the basis was extended to the 134 M_J components of the ${}^8S$ and ${}^6(P,I,D)$ free-ion levels. For this caclulation, $B_0^4 = -2160.0$ cm^{-1} and $B_0^6 = 792.85$ cm^{-1}, and the mean error is reduced to about 0.5 cm^{-1}. This calculation predicts the correct order of the ground-state levels and gives an over-all ground-state splitting of about one-half the experimental splitting. The calculated ground-state splitting does not change when the basis is further extended to include all higher free-ion levels containing ${}^6G$ character. We conclude that a good crystal-field calculation for Gd^{3+} is possible and depends strongly on the quality of the free-ion states.

INTRODUCTION

THE observed optical spectra of Gd^{3+} in crystals consist of absorption and emission lines between the ground state ${}^8S_{7/2}$ and the nearest excited multiplets ${}^6P$, ${}^6I$, ${}^6D$. The first interpretation of the optical spectra of Gd^{3+} was done by Dieke and Leopold[1] and later extended by Hellwege, Hufner, and Schmidt.[2] The spectra of Gd^{3+} in fluorite lattices have been investigated by Makovsky,[3] Gilfanov *et al.*,[4,5] Schlesinger and Whippey,[6] Yaney and Donlan,[7] and most recently by Detrio.[8] The crystal spectrum of Gd^{3+}:$LaCl_3$ has been analyzed by Piksis, Dieke, and Crosswhite.[9] In addition, theoretical calculations have been carried out on the ${}^6(P, I, D)$ multiplets by Runciman,[10] Wybourne,[11] Judd,[12] and Judd, Crosswhite, and Crosswhite.[13]

The spectrum of CaF_2:Gd^{3+} is composed of lines which originate from the various symmetry sites which are allowed by charge compensation mechanisms when a Gd^{3+} ion is substituted into the lattice for a Ca^{2+} ion. In analyzing the spectra, one must determine which transitions are associated with which symmetry site. This has been done by Makovsky[3] and Gilfanov *et al.*[4,5] for transitions between the ${}^6P$ multiplets and the ground state. Recently, Detrio,[8] by means of Zeeman studies, has identified the irreducible representations of the Stark manifolds of the ${}^6P_{7/2}$ and ${}^6P_{5/2}$ levels in a cubic symmetry site. It is, therefore, of interest to perform a crystal-field calculation using the ${}^6P_{7/2}$ and ${}^6P_{5/2}$ splittings to fit the crystal coefficients of the octahedral field.

The electronic configuration f^7 to which the ions Gd^{3+}, Eu^{2+}, and Tb^{4+} belong is the most complex configuration encountered in atomic spectroscopy. The electronic configuration f^7 is a half-filled shell and thus gives no first-order interactions in the crystal field for a purely Russell-Saunders coupled state.[14] In order to do a good crystal-field calculation for Gd^{3+}, one must first obtain a set of accurate intermediate coupled free-ion-state vectors.[10–13] This was done by calculating the free-ion states using essentially the method of Judd *et al.*,[13] who have demonstrated the importance of including spin-other-orbit and spin-spin effects in the Hamiltonian.

For the f^7 configuration there are 3432 Slater-determinantal states allowed by the Pauli exclusion principle. It is evident that exact calculations on this configuration are impossible, owing to the huge matrices that would be involved. Some approximations must be used; in particular, it is necessary at some point to ignore a majority of the states. Hopefully, the number of states having the most influence on the observable levels is small enough to give reasonably sized matrices. According to our calculations, this hope is realized.

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FREE-ION CALCULATIONS

The calculations are done in two steps. In the first step, the free-ion wave functions are computed. The 3432 Slater states are coupled by the Russell-Saunders scheme to form 3432 Russell-Saunders states (hereafter called RS states) in the scheme $|f^7\tau SLJM_J\rangle$. These states are used as a basis for the free-ion calculation. The free-ion Hamiltonian used is

$$H_f=H_e+H_{so}+\alpha L(L+1)+H_{soo}+H_{ss}. \tag{1}$$

The first term H_e is the Coulomb repulsion interaction $\sum_{i<j} e^2/r_{ij}$. The matrix elements of this interaction between RS states are diagonal in S, L, J, and M_J and are tabulated by Nielson and Koster[15] in terms of Racah's electrostatic parameters[16] E^0, E^1, E^2, and E^3. The second term H_{so} is the spin-orbit interaction $\zeta(4f)\sum_i \mathbf{s}_i\cdot\mathbf{l}_i$. Its matrix elements are diagonal in J and M_J and are tabulated in reduced form by Nielson and Koster.[15] The third term $\alpha L(L+1)$ is the lowest-order correction for configuration interaction.[17] The fourth and last terms in Eq. (1), H_{soo} and H_{ss}, are the spin–other-orbit and spin-spin interactions, respectively. Equivalent operator factors for H_{soo} and H_{ss} suitable for RS coupled states (i.e., diagonal in S, L, J, and M_J) are tabulated by Judd[12] and Judd *et al.*,[13] for the sextet levels of f^7 in terms of Marvin's[18] integrals M^0, M^2, and M^4. The equivalent operators are[13]

$$H_{soo}=\lambda'\mathbf{L}\cdot\mathbf{S},$$

$$H_{ss}=-\rho[(\mathbf{L}\cdot\mathbf{S})^2+\tfrac{1}{2}\mathbf{L}\cdot\mathbf{S}-\tfrac{1}{3}L(L+1)S(S+1)].$$

The values of the parameters reported by Judd *et al.*[13] were used in this free-ion calculation. The free-ion calculation is complete in that no approximations are used in diagonalizing H_f.

CRYSTAL-FIELD CALCULATION

The free-ion state vectors serve as basis vectors for the second step of the calculation, the crystal-field interaction. The crystal-field Hamiltonian for octahedral symmetry (which is the symmetry of the CaF_2 lattice surrounding the Gd^{3+} ions in cubic sites) is

$$\begin{aligned}H_{cf}=B_0{}^4[C_0{}^{(4)}+(5/14)^{1/2}(C_4{}^{(4)}+C_{-4}{}^{(4)})]\\+B_0{}^6[C_0{}^{(6)}-(\tfrac{7}{2})^{1/2}(C_4{}^{(6)}+C_{-4}{}^{(6)})],\end{aligned} \tag{2}$$

where $B_0{}^4$ and $B_0{}^6$ are coefficients determined by the charge distribution of the surrounding lattice and by the radial integrals of the f^7 electrons, and the $C_q{}^{(k)}$ are tensor operators which are proportional to spherical harmonics,

$$C_q{}^{(k)}=[4\pi/(2k+1)]^{1/2}Y_{kq}.$$

The crystal field H_{cf} destroys rotational symmetry; so J and M_J are no longer good quantum numbers. The matrix elements of H_{cf} are, however, diagonal in the crystal quantum number μ of Hellwege.[19] For octahedral symmetry, $\mu=\frac{1}{2}$, connecting states having $M_J=\pm\frac{1}{2}\pm4n$, and $\mu=\frac{3}{2}$, connecting states having $M_J=\pm\frac{3}{2}\pm4n$, where n is an integer. Hence, the matrix of H_{cf} breaks up into two essentially equal sized submatrices, one for $\mu=\frac{1}{2}$ and the other $\mu=\frac{3}{2}$. Owing to Kramers's theorem,[20] each of these submatrices can be block diagonalized into two identical independent matrices corresponding to invariance of the system under time inversion (complex conjugation). These are the only simplifications possible, however, under the symmetry group of the crystal field. Thus, the crystal-field matrix for the f^7 configuration can be reduced only to four submatrices, each of rank 858. Such matrices are much too large to diagonalize even with today's largest and fastest computers. At this point, we then have to make simplifications, thereby leading to an inexact calculation.

The simplest approximation to make is to ignore all but a few states, i.e., diagonalize a much smaller matrix. The states left out can then be approximately taken into account by a perturbation calculation. In our first calculation, only the ${}^6P_{7/2}$, ${}^6P_{5/2}$, and ${}^6P_{3/2}$ states were diagonalized. Next, the ${}^8S$, ${}^6P$, ${}^6I$, and ${}^6D$ multiplets were diagonalized. Finally, the ${}^8S$, ${}^6P$, ${}^6I$, ${}^6D$ multiplets and all other free-ion states having more than 4% ${}^6G$ composition were diagonalized. The reasons for these choices and the results of the calculations are discussed in the "Results and Discussion" section.

FITTING PROCEDURE

The rank of the matrix of the crystal-field interaction, Eq. (4), will depend on the number of free-ion states one wishes to use for a basis. Imbedded in any matrix one calculates, however, are the unknown parameters $B_0{}^4$ and $B_0{}^6$ which depend on the lattice parameters and radial integrals of the f^7 charge distribution. Since the $B_0{}^4$ and $B_0{}^6$ cannot be calculated from first principles without accurate dynamical wave functions, the $B_0{}^4$ and $B_0{}^6$ coefficients are fit to the experimental data by what is essentially a least-squares method. Initial values are assumed for the $B_0{}^4$ and $B_0{}^6$, the eigenvalues that result from diagonalization of the crystal-field matrix are compared with experimental energies, appropriate adjustments in the coefficients are made, the matrices recalculated and rediagonalized, and the comparison is made again. This iterative process is carried out until the best possible agreement is obtained between the calculated and

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experimental splittings. The calculation is accomplished by a computer program based on a method due to Nelder and Mead[21] for minimization of a function of several variables. The function minimized was

$$F(B_0^4,B_0^6)=\sum_{i=1}^{n} W_i[\Delta\lambda_i(B_0^4,B_0^6)-\Delta E_i]^2,$$

where $\Delta\lambda_i$ is the calculated splitting of the ith Stark component from the calculated center of gravity for given values of B_0^4 and B_0^6, ΔE_i is the experimental splitting of the ith Stark component from the experimental center of gravity, and W_i is a weighing factor. In this case $W_i=1$ for the Stark components of ${}^6P_{7/2}$ and ${}^6P_{5/2}$ and $W_i=0$ for all others. The program then finds a local minimum with respect to the parameters B_0^4 and B_0^6, given initial values for B_0^4 and B_0^6. It is, of course, possible to find more than one local minimum depending on one's initial choices for B_0^4 and B_0^6. For this particular problem, however, only one physically acceptable minimum was found.

RESULTS AND DISCUSSION

It was first attempted to calculate the crystal-field matrix and fit B_0^4 and B_0^6 using only the multiplet states of the ${}^6P$ group as a basis. This means that the fitting routine requires an iterative rediagonalization of a 4×4 matrix for the $\mu=\frac{1}{2}$ crystal quantum number and a 5×5 matrix for the $\mu=\frac{3}{2}$ crystal quantum number. The results of the calculation gave

$$B_0^4=-2270.79 \text{ cm}^{-1},\quad B_0^6=730.65 \text{ cm}^{-1},$$

or in terms of the more familiar operator equivalent technique coefficients[22]

$$A_4^0\langle r^4\rangle=-283.85 \text{ cm}^{-1},\quad A_6^0\langle r^6\rangle=45.67 \text{ cm}^{-1}.$$

The minimum value of the sum of the squares of the residuals, $F(B_0^4,\ B_0^6)$, in this case was found to be 307.29 cm^{-2}, which gives a mean error of roughly 8 cm^{-1} for a particular Stark splitting. A comparison of the theoretical and experimental Stark manifolds for this calculation is given in Fig. 1. It is seen that this calculation does not give very satisfactory agreement with experimental.

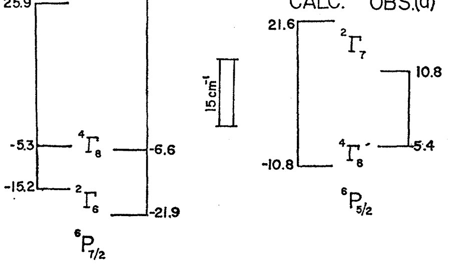

FIG. 1. Comparison of observed and calculated splittings from the center of gravity when only the ${}^6P$ multiplets are used as a basis. (a) See Ref. 8.

To improve the quality of the fit, the number of free-ion basis states was increased in such a way that all experimentally observed free-ion multiplets ${}^8S$, ${}^6(P,\ I,\ D)$ were included in the second calculation. These multiplets are only four of the 119 $|f^7\tau SL\rangle$ Racah states required to classify the f^7 configuration, and they yield only 15 of the 327 possible states $|f^7\tau SLJ\rangle$ which arise from the spin-orbit coupling of the Racah states. It initially seems logical to limit the extension of the basis to these multiplets if for no other reasons than practicality of calculation and that these are the only multiplets that have been observed and identified to date.[1–9]

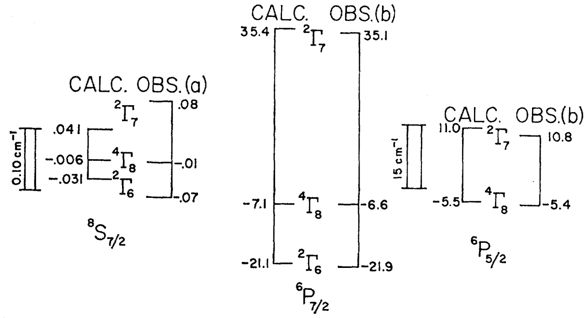

FIG. 2. Comparison of observed and calculated splittings from the center of gravity using the extended basis. (a) See Refs. 24–26. (b) See Ref. 8.

With the inclusion of the additional basis states, the fit then requires the iterative rediagonalization of a 34×34 matrix for the $\mu=\frac{1}{2}$ crystal quantum number and a 33×33 matrix for the $\mu=\frac{3}{2}$ crystal quantum number. The crystal-field parameters were then found to be

$$B_0^4=-2160.0 \text{ cm}^{-1},\quad B_0^6=792.85 \text{ cm}^{-1},$$

or again in terms of the operator equivalent parameters

$$A_4^0\langle r^4\rangle=-270.0 \text{ cm}^{-1},\quad A_6^0\langle r^6\rangle=49.55 \text{ cm}^{-1}.$$

The value of the sum of the squares of the residuals was 1.27 cm^{-2} giving a mean error of about 0.5 cm^{-1} between the observed and calculated splittings. It is seen that the value of the crystal parameters is not sharply altered by the inclusion of these higher-order effects (i.e., the extension of the basis); however, the improvement in the quality of the fit is quite remarkable as demonstrated by Fig. 2. Inclusion of the ${}^8S$, ${}^6(P,I,D)$ multiplets takes account of J mixing from these levels and it is seen that this accounts for a shift in the center of gravity of 63.1 cm^{-1} in the ${}^6P_{7/2}$ level as compared to the over-all splitting of 56.5 cm^{-1} in the ${}^6P_{7/2}$ level. A similar shift is noted in the ${}^6P_{5/2}$ center of gravity.

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This shift of the centers of gravity is in the proper direction so as to bring closer agreement between the calculated and experimentally observed centers of gravity of the crystal splittings. The calculated center of gravity of the $^6P_{7/2}$ level is within 11.5 cm^{-1} of the observed center of gravity, and the calculated value for the $^6P_{5/2}$ level is within 3.1 cm^{-1} of the observed value. (See Table I. It is significant to note that no attempt was made to obtain agreement between the calculated and observed centers of gravity when fitting the experimental data.) The values obtained for the cubic-crystal-field coefficients of Gd^{3+} compare with those of other trivalent rare-earth ions in CaF$_2$. Weber and Bierig[23] have indicated the range of these values to be

$$A_4^0\langle r^4\rangle \sim -(250\text{–}430)\ \text{cm}^{-1},\quad A_6^0\langle r^6\rangle \sim (30\text{–}45)\ \text{cm}^{-1}.$$

TABLE I. Comparison of calculated and observed cubic-field Stark components in CaF$_2$:Gd^{3+}.

Term	Representation	Calculated energy (cm^{-1})	Observed energy[a]	Calculated center of gravity	Observed center of gravity
$^6P_{7/2}$	$^2\Gamma_6$	32 025.16	32 035.8	32 046.28	32 057.7
	$^4\Gamma_8$	32 039.15	32 051.1		
	$^2\Gamma_7$	32 081.64	32 092.8		
$^6P_{5/2}$	$^4\Gamma_8$	32 640.70	32 637.6	32 646.19	32 643.0
	$^2\Gamma_7$	32 657.16	32 653.8		

[a] See Refs. 3–5, and 8.

TABLE II. Stark energies of the ^8S, $^6(P, I, D)$ multiplets for cubic symmetry in CaF$_2$:Gd^{3+}.

Free-ion state	Calculated free-ion energy (cm^{-1})	Calculated Stark components	Representation
$^8S_{7/2}$	0.273	0.0	$^2\Gamma_6$
		0.025	$^4\Gamma_8$
		0.072	$^2\Gamma_7$
$^6P_{7/2}$	32 109.62	32 025.16	$^2\Gamma_6$
		32 039.15	$^4\Gamma_8$
		32 081.64	$^2\Gamma_7$
$^6P_{5/2}$	32 721.87	32 640.70	$^4\Gamma_8$
		32 657.16	$^2\Gamma_7$
$^6P_{3/2}$	33 274.62	33 190.13	$^4\Gamma_8$
$^6I_{7/2}$	35 855.87	35 827.96	$^2\Gamma_6$
		35 852.78	$^4\Gamma_8$
		35 951.65	$^2\Gamma_7$
$^6I_{9/2}$	36 198.56	36 162.61	$^2\Gamma_6$
		36 176.99	$^4\Gamma_8$
		36 249.58	$^4\Gamma_8$
$^6I_{17/2}$	36 259.22	36 260.57	$^2\Gamma_6$
		36 260.87	$^4\Gamma_8$
		36 267.16	$^4\Gamma_8$
		36 284.09	$^2\Gamma_6$
$^6I_{17/2}$	36 259.22	36 295.28	$^2\Gamma_7$
		36 302.84	$^4\Gamma_8$
$^6I_{11/2}$	36 469.22	36 430.80	$^4\Gamma_8$
		36 441.71	$^2\Gamma_7$
		36 521.67	$^4\Gamma_8$
		36 532.17	$^2\Gamma_6$
$^6I_{15/2}$	36 585.06	36 545.82	$^4\Gamma_8$
		36 553.94	$^2\Gamma_6$
		36 611.27	$^4\Gamma_8$
		36 614.23	$^2\Gamma_7$
		36 643.12	$^4\Gamma_8$
$^6I_{13/2}$	36 617.50	36 577.28	$^4\Gamma_8$
		36 582.48	$^2\Gamma_7$
		36 648.90	$^2\Gamma_7$
		36 669.68	$^2\Gamma_6$
		36 694.99	$^4\Gamma_8$
$^6D_{9/2}$	39.551.85	39 450.32	$^4\Gamma_8$
		39 605.24	$^4\Gamma_8$
		39 637.78	$^2\Gamma_6$
$^6D_{1/2}$	40 476.34	40 460.40	$^2\Gamma_6$
$^6D_{7/2}$	40 603.95	40 595.32	$^4\Gamma_8$
		40 617.56	$^2\Gamma_6$
		40 629.87	$^2\Gamma_7$
$^6D_{3/2}$	40 743.35	40 761.74	$^4\Gamma_8$
$^6D_{5/2}$	40 901.56	40 895.10	$^4\Gamma_8$
		41 003.86	$^2\Gamma_7$

The results of the calculation for all multiplets are summarized in Table II, and Fig. 2 shows the comparison between the experimental and calculated splittings of the $^8S_{7/2}$, $^6P_{7/2}$, and $^6P_{5/2}$ levels. It is seen that this calculation does yield a splitting for the somewhat perplexing $^8S_{7/2}$ ground state of Gd^{3+}. The ordering of the Stark components is the same as that observed in the EPR studies of Title[24] and Shuskus,[25] that is, the correct sign is obtained. The over-all splitting of 0.072 cm^{-1} is less than the over-all experimentally observed splitting of 0.149 cm^{-1}.[24–26] However, the value of the reduced matrix elements that one obtains appears to be quite sensitive to the quality of the free-ion state vectors, especially in the ground state. Wybourne[11] has demonstrated a strong dependence of the ground-state reduced matrix elements on the value of the spin-orbit parameter that one chooses in obtaining the free-ion state vectors. Wybourne, after considering several different mechanisms which could explain the ground-state splitting, suggests that only a detailed interaction of the Gd ion with its ligands may be able to explain the splitting of the ground state. However, it is seen here that, for cubic symmetry at least, a significant part of the splitting is accounted for by using good-quality free-ion state vectors. It is suggested that further refinement of the free-ion state vectors may improve the ground-state calculation even more. Before attempting to improve upon the free-ion wave functions, however, another possible source of the remaining splitting of the ground state was explored in a third calculation. It was noticed that when the splitting of the $^8S_{7/2}$ multiplet was calculated to first order in the crystal field, i.e., with no J mixing from higher-lying multiplets, the splitting obtained was 0.058 cm^{-1}. When J mixing of the $^6(P, I, D)$ was included, the splitting obtained was 0.072 cm^{-1}. Therefore, J mixing of the $^6(P, I, D)$ multiplets accounts for about 19% of the calculated ground-state splitting. It was thus felt that the basis states of the calculation should be extended to include most of the remaining sextet multiplets $^6(G, H, F)$ and the lowest quartets in order to determin

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their effect upon the ground state. The criterion for selecting the extended basis states was to include those vectors with significant ^6G composition (greater than 4%), since the major interactions between ground and excited states involves excited-state ^6G components only. Examination of the composition of the ground-state vector and all higher-lying multiplets indicates that the J-mixing contribution to the ground splitting from any other multiplets should be negligible.

No attempt was made to fit the data with this extended basis, since the matrices are so large. We merely assumed the previously calculated values of B_0^4 and B_0^6 and computed the crystal-field matrices with the extended basis and diagonalized them. This, of course, causes the quality of the previous fit to deteriorate somewhat; however, it was too slight to justify attempting a new fit with such large matrices, especially since we were seeking an effect in the ground state. The effect, unfortunately, did not appear. The over-all splitting of the ground state was only increased from 0.072 to 0.074 cm^{-1}. Thus, we were able to account for about half of the ground-state splitting with a calculation which is good to all orders within the basis used. It is felt then that further investigation of the ground-state free-ion state vector is merited.

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Spin-Lattice Relaxation in Periodically Perturbed Systems*

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Spin-lattice relaxation theory is examined, in the perturbation-theory regime, for nuclear spin systems which experience time-dependent forces not only from fluctuating spin-lattice interactions but also from externally produced periodic disturbances. These include strong steady rf fields (spin-locking and the Lee-Goldburg experiments), amplitude and phase-modulated rf fields (pulsed narrowing experiments), and modulation of the secular dipolar fields through rotation of the sample. It is shown for relatively slow molecular motions ($T_2>\tau\gg\omega_0^{-1}$, where T_2 is the relaxation time, τ the correlation time, and ω_0 the rf frequency) that uncoupled Bloch equations can be obtained for suitably defined components of the magnetization. The spin-lattice relaxation times, which limit the degree of narrowing that can be obtained, depend in every case on Fourier components of the thermal motion in the neighborhood of the frequency of the periodic disturbance, and are of the same order of magnitude for all the experiments. Various narrowing experiments on substances having molecular motion are discussed.

I. INTRODUCTION

In recent years, a number of magnetic resonance experiments have been developed in which the behavior of the spins is influenced in an important way by a strong perturbation which is periodic in time. We have in mind the resonant spin locking[1,2] and Lee-Goldburg (LG) experiments,[3] in which the perturbation is a rf magnetic field applied on or off resonance; various multiple-pulse experiments,[4–8] in which a similar field is amplitude and/or phase modulated by a pulse train; and the sample-spinning experiments,[9–11] where a field inhomogeneity or an internal local field is modulated by rotating the sample with respect to the Zeeman field.

All these experiments have in common that, in a suitable frame of reference, some or all of the secular terms of the internal Hamiltonian become time-dependent and very often much less effective for spin-spin relaxation. It can be shown[8] that the secular decay of magnetization becomes describable by a weaker effective time-independent Hamiltonian. Therefore, speaking in terms of the Fourier transform of the decay, we may say that the periodic disturbance provides a means of line narrowing. Perhaps with the exception of the first one, all of the above-mentioned experiments have been motivated by this very fact and, correspondingly, have been treated theoretically and exploited

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