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Microscopic Analysis of Exchange and Motional Narrowing

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From a microscopic analysis of the paramagnetic resonance line, the exchange- and motional-narrowing phenomena are shown to be basically distinct. Exchange-narrowed lines are essentially made up of the Fourier transform of the cross-correlation functions; motional-narrowed lines are only formed by the Fourier transform of the self-correlation function.

In this paper, we wish to discuss the well-known phenomenon of the narrowing of paramagnetic resonance lines. This effect is caused by the exchange interactions between spins in solids or by the motions of the atoms or molecules which carry the spin in liquids. Usually, the theory is investigated from a macroscopic treatment of the correlation function, whose frequency Fourier transform gives the spectral resonance line. The most complete theory had been given by Kubo and Tomita.[1] These authors use a perturbation expansion, and in one general formalism they can explain both the exchange and the motional narrowing. The mathematical property which leads to this result is the fact that the Hamiltonian operators of the exchange or motional interactions, E and M, respectively, commute with the components $\alpha = x, y, z$ of the total spin

$$\vec{S} = \sum_i \vec{s}_i , \tag{1}$$

$\vec{s}_i$ being an individual spin:

$$\left[S^\alpha , \begin{Bmatrix} E \\ M \end{Bmatrix} \right] = 0 . \tag{2}$$

Thus, the understanding of these two phenomena is apparently quite the same. The exchange in solids causes rapid motion in the spin system, which produces an averaging out of the effects of the broadening interactions such as magnetic dipolar interactions. In a roughly similar way, the temperature motion of atoms in liquids reduces the local magnetic field seen by each spin $\vec{s}_i$. However, this microscopic explanation must be carefully examined. One can obtain knowledge about the motion of an individual spin by studying the spectral function of the resonance line, not from a macroscopic point of view but from a microscopic analysis.

For N identical spins, the paramagnetic resonance line is given by the frequency Fourier transform $F(\omega)$ of the macroscopic correlation function

$$G(t)=\langle e^{iFt/\hbar}\, S^x e^{-iFt/\hbar}\, S^x\rangle/\langle S^{x^2}\rangle \; . \tag{3}$$

The interactions between spins are represented by the Hamiltonian F. For solids, it is $F=D^0+E$ and for liquids, $F=D^0+M$, where D^0 is the secular part of the magnetic dipolar spin-spin interactions. Since we only want to concentrate our attention on the narrowing phenomenon, we will not take into account the nonsecular dipolar Hamiltonians and consequently we ignore the "$\frac{10}{3}$ effect."

In order to express $G(t)$ by microscopic correlation functions, we insert (1) in Eq. (3):

$$G(t)=\sum_{i,j=1}^{N}\langle e^{iFt/\hbar}\, s_i^x e^{-iFt/\hbar}\, s_j^x\rangle/\sum_{i=1}^{N}\langle s_i^{x^2}\rangle \; . \tag{4}$$

Now, one can distinguish between the self-correlation ($i=j$) and the cross-correlation ($i\neq j$) functions of the individual spins. The correlation function of the spin labeled 0 is defined by

$$g_{0,i}(t)=\langle e^{iFt/\hbar}\, s_0^x e^{-iFt/\hbar}\, s_i^x\rangle/\langle s_i^{x^2}\rangle \; , \tag{5}$$

the Fourier transform of which is $f(0, i;\, \omega)$. Since all the spins are identical, the Fourier transform of Eq. (4) which gives the resonance line becomes

$$F(\omega)=f(0,0;\,\omega)+\sum_{i\neq 0} f(0,i;\,\omega). \tag{6}$$

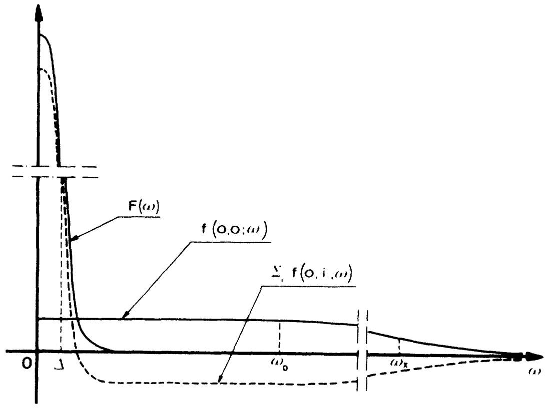

FIG. 1. Full curves are the narrowed line shape $F(\omega)$ and the Fourier transform of the self-correlation function $f(0,0;\omega)$. The dashed curve represents the sum of the Fourier transform of the cross-correlation functions $f(0,i;\omega)$. Arbitrarily we have chosen $\omega_x\simeq 10\omega_d$; then $\Delta\simeq\omega_d/10$.

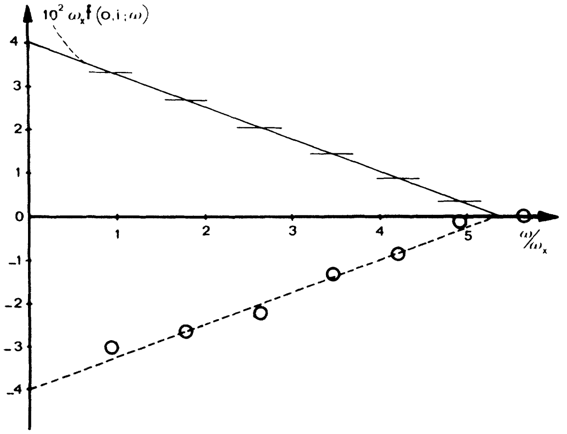

FIG. 2. Full curve is the Fourier transform of the self-correlation function given by Carboni and Richards (Ref. 2) and the dashed curve is its opposite. The plots (open circle) show the contribution of the first four Fourier transforms of the cross-correlation functions.

Therefore, in any case, the resonance line is made up of one self-correlation function together with all the cross-correlation functions. Without the narrowing Hamiltonians, each of these correlations contributes to the spectral line $F(\omega)$, the width of which is of the order of $\omega_d\sim\langle D_0^2\rangle^{1/2}$. We must ask now what is the role of these correlations in the presence of E or M.

In solids, when the exchange Hamiltonian E is much larger than D^0, $F(\omega)$ is narrowed. The linewidth becomes $\Delta\simeq\omega_d^2/\omega_x$, where $\omega_x\sim\langle E^2\rangle^{1/2}$. On the other hand, $f(0,0;\omega)$ is expected to exhibit some components at very high frequency (the Overhauser effect observed in insulators gives a proof of this: There are components at $\omega\sim\omega_e$, the electronic Larmor frequency). Roughly speaking, the characteristic width of $f(0,0;\omega)$ is ω_x. Now, we notice that from the definition of the Fourier transform we can deduce the following properties:

$$\int_{-\infty}^{+\infty} d\omega\, F(\omega)=\int_{-\infty}^{+\infty} d\omega f(0,0,\omega)=1 \; .$$

Since the areas of $F(\omega)$ and $f(0,0;\omega)$ are equal, the amplitude of $f(0,0;\omega)$ will be very small. In Fig. 1 we have reconstituted $F(\omega)$ from Eq. (6). The full curves are $F(\omega)$ and $f(0,0;\omega)$. Consequently, the dashed line represents the sum of all the cross-correlation spectra, that is, $\sum_{i(\neq 0)}f(0,i;\omega)$

On this scheme we see clearly that the paramagnetic resonance line $F(\omega)$ expresses only the cross-correlation effects and that for $\omega>\Delta$ the contribution of the cross correlation exactly cancels the contribution of the self-correlation. This fact can be illustrated from the correlation functions calculated by Carboni and Richards.[2] These authors have performed numerical calculations in the case of linear exchange chains. Indeed, the spin motion is only due to the exchange Hamiltonian E. But for the present purpose, in the high-frequency range ($\omega > \omega_x$), their results may be regarded as being still valid because D^0 only affects the low-frequency range. Figure 2 shows the sum $\sum f(i, 0; \omega)$ restored from the frequency Fourier transform of the first four cross-correlation functions ($i = -4 \cdots +4$) (Fig. 4 of Ref. 2) and the self-correlation function $f(0, 0; \omega)$ (Fig. 5 of Ref. 2). Their contributions are equal and opposite. Therefore, the other cross-correlation functions must have a negligible influence.

In liquids, the motion Hamiltonian M of the atoms or molecules is defined by coordinates which are different from those of the spins. Thus, in the case of an individual spin, a commutation rule equivalent to (2) is still valid:

$$[s_i^\alpha, M] = 0 \ .$$

Therefore, the self-correlation spectrum $f(0, 0; \omega)$ is narrowed in the same way as $F(\omega)$, and in the case of an extreme narrowing the contribution of the cross correlation becomes quite negligible.

In conclusion, the macroscopically identical behavior of the paramagnetic resonance line, under the influence of either exchange or motion, masks two quite distinct phenomena. In solids with exchange interactions the line shape is due to the correlations of one spin with all the others. On the contrary, in liquids the line shape comes from the self-correlation of one spin: The motion completely "decorrelates" the spins amongst themselves.

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Paramagnetic Spin-Lattice Relaxation via the Anharmonic Raman Process*

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The anharmonic Raman process, which was shown by Van Kranendonk and Walker to be important in the case of nuclear quadrupolar relaxation, is shown here to be of sufficient magnitude to explain the Raman relaxation rates of the paramagnetic ions Cr^{3+} and Ni^{2+} in MgO. This new relaxation process involves the anharmonic three-phonon interaction.

The theory of the spin-lattice relaxation of paramagnetic ions in insulating crystals has recently been reviewed by Stevens[1] and by Abragam and Bleaney.[2] Many of the more important original papers on the subject are contained in the book edited by Manenkov and Orbach.[3] It is evident from these articles that a major assumption of previous theories which has not been seriously questioned up to the present is that the phonons can be treated in the harmonic approximation. Recently, however, Van Kranendonk and Walker[4] showed that a new relaxation process, which they called the anharmonic Raman process, and which depends for its existence on the anharmonic three-phonon coupling, is important in the theory of nuclear quadrupolar relaxation. More recently still, two papers[5,6] concerned with the derivation of the rate equations describing spin-lattice relaxation in anharmonic crystals have confirmed the existence of the anharmonic Raman process described by Van Kranendonk and Walker. There are as yet, however, no estimates of the magnitudes of the relaxation rates predicted by this process for paramagnetic ions. The purpose of this paper is to show that the anharmonic Raman process predicts relaxation rates having magnitudes comparable to those observed in the cases of $MgO : Ni^{2+}$ and $MgO : Cr^{3+}$. The main conclusion is thus that the anharmonic Raman process deserves serious consideration as a possible relaxation mechanism for paramagnetic ions in crystals.

The Feynman diagram corresponding to the anharmonic Raman process is shown in Fig. 1(a), and a somewhat different pictorial view of the same process is shown in Fig. 2. An explicit mathematical description of the anharmonic Raman process will be given below.

In their analysis of nuclear quadrupolar relaxation, Van Kranendonk and Walker showed that the