Correlated ESR and NMR line-broadening effect associated with external-magnetic-field inhomogeneities

Sook Lee and D. C. Power
Department of Physics, Saint Louis University, St. Louis, Missouri 63103
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The unusual dynamic nuclear polarization (DNP) phenomena at the center of an inhomogeneously broadened ESR line arising from a correlated ESR and NMR line broadening have been investigated for the case of inhomogeneous external magnetic fields. It was found that DNP experimental data obtained for the central Cr^{3+} ESR and ^{27}Al NMR lines in a single crystal of ruby were consistent with the phenomenological model developed for the correlated ESR and NMR line broadenings arising from the strain and c-axis-variation effects. This result can be taken as a direct verification of the phenomenological model.

I. INTRODUCTION

Based on ordinary theory of dynamic nuclear polarization (DNP) by the solid effect[1] in single-crystalline solids exhibiting an inhomogeneously broadened electron spin resonance (ESR) line, it was predicted that the enhancement of the nuclear magnetic resonance (NMR) signal would be proportional to the negative of the first derivative of the ESR absorption line shape. Thus a vanishing NMR enhancement was expected under DNP produced by saturating the center portion of the inhomogeneous ESR line where the first derivative vanishes. However, it was found that not only did the enhancement of the NMR signal not vanish, but the NMR line shape changed dramatically under DNP at the center of the ESR line resulting from a correlation between the ESR and NMR inhomogeneous line broadenings.[2,3] Subsequently a quantitative phenomenological model was developed first for the correlated inhomogeneous line broadenings due to variations in the ESR and NMR coupling constants caused by strains from crystalline imperfections (the strain effect).[4,5] This work represented the first method of detecting and investigating a correlated ESR-NMR line-broadening effect in single crystals. The phenomenological treatment was later extended to include the case where the correlated ESR and NMR line broadenings arise from variations in the directions of the ESR and NMR symmetry axes (and c-axis-variation effect).[6]

In the present paper, we describe the results of our investigation extending the phenomenological model to the case where the correlated ESR and NMR line broadenings are due to inhomogeneities in the external magnetic field. Treatment of this case is important because it provides a method by which one can directly verify the validity of the phenomenological model employed in the analyses of the correlated strain and c-axis-variation effects. The ESR-NMR systems used in this investigation were the Cr^{3+} $M = +\frac{1}{2} \leftrightarrow -\frac{1}{2}$ ESR line and the ^{27}Al $m = +\frac{1}{2} \leftrightarrow -\frac{1}{2}$ NMR line in a single crystal of pink ruby. As is well known,[7,8] in ruby these lines are well separated from the satellite ESR and NMR component lines arising from the ESR fine-structure and the NMR quadrupole-structure splittings, respectively. In addition, they are practically free from the strain and c-axis-variation effects so that the inhomogeneous-magnetic-field effect can be readily isolated and investigated.

II. THEORETICAL

The qualitative features of the correlated ESR and NMR line-broadening effect associated with inhomogeneous external magnetic fields under DNP at the center of the ESR line can be seen in the following manner. Assume that the crystal is composed of three parts, each part subjected to slightly different magnetic fields, H_1, H_2, and H_3. For a constant microwave frequency, the ESR spectrum arising from the whole sample would consist of three ESR lines centered at the three different magnetic fields as illustrated in Fig. 1(a). We consider that each ESR line is inhomogeneously broadened by unresolved electron-nuclear hyperfine interactions in the crystal, and that the resultant DNP of the solid effect is proportional to the negative of the first derivative of each ESR line (the normal solid effect).[1] Figure 1(b) shows the NMR spectrum, which consists of three lines centered at the three different NMR frequencies ν_1, ν_2, and ν_3 corresponding to H_1, H_2, and H_3. Each NMR line is assumed to be broadened by the nuclear-nuclear and electron-nuclear interactions.

When the center portion of the envelope of the three ESR lines in Fig. 1(a) is saturated by a strong microwave field, the high-field side of the ESR line centered at H_1, the center portion of the ESR line at

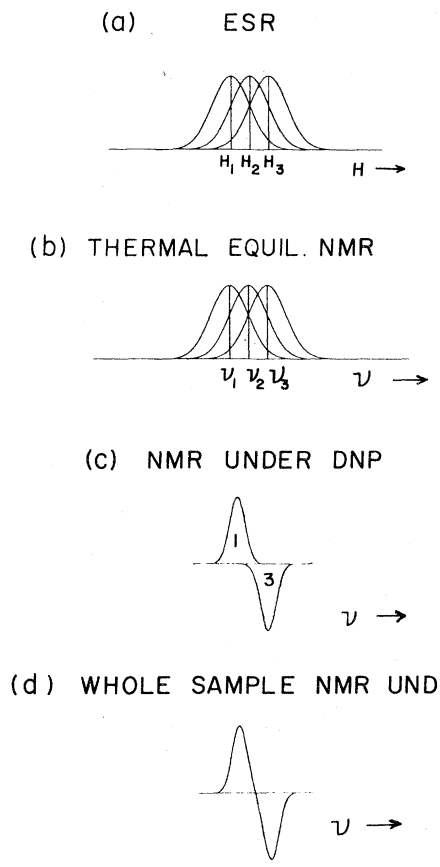

FIG. 1. Qualitative behavior of the NMR line shape under DNP at the center of an ESR line broadened by magnetic-field inhomogeneities.

H_2, and low-field side of the ESR line at H_3 will all be simultaneously saturated. It follows from the normal solid effect that the NMR signal from the nuclear spins in the first part of the sample will be positively enhanced, the signal from the nuclear spins in the third part of the sample will be negatively enhanced, and the signal from the center part of the sample will vanish [see Fig. 1(c)]. The resultant whole-sample NMR signal is illustrated in Fig. 1(d), which indicates that the NMR absorption line under DNP at the center of the ESR envelope from the whole sample approximates the positive first derivative of the envelope of the thermal-equilibrium NMR lines.

The above field-inhomogeneity effect can be treated quantitatively in the same manner as the strain[4] and c-axis-variation[6] effects. In perfectly homogeneous fields, the ESR line of the paramagnetic ions is assumed to be inhomogeneously broadened by unresolved hyperfine interactions with a Gaussian line shape of width ΔH_0, centered at $H = H_0$. In inhomogeneous magnetic fields, the resonance field of each paramagnetic ion is shifted by an amount h. Assuming that these field shifts are distributed according to a Gaussian function having a width Δh, the resultant ESR line shape will be the convolution of two Gaussian functions, and the total line width will be

$$\Delta H = (\Delta H_0^2 + \Delta h^2)^{1/2} \ . \tag{1}$$

It should be noted that the broadening due to magnetic-field inhomogeneities is the same for all $M \leftrightarrow M-1$ ESR transitions when $S \geq 1$.

Surrounding each paramagnetic ion there is a shell of influence in which the nuclear spins are assumed to be dynamically polarized only by this ion. Considering the most general case where the magnetic fields vary within the shells of influence, the distribution of NMR frequencies of the nuclear spins in the shell is given by a Gaussian function, centered at their average NMR frequency $\bar{\nu}$ with width $\delta\nu$. There is also the variation of the average NMR frequencies from shell to shell within the sample, and this variation is also assumed to be described by a Gaussian function of width $\delta\bar{\nu}$. The total contribution of the magnetic-field inhomogeneities to the whole sample NMR linewidth is

$$\Delta\nu = (\delta\nu^2 + \delta\bar{\nu}^2)^{1/2} \ . \tag{2}$$

Including the intrinsic linewidth due to the rigid lattice nuclear-nuclear and electron-nuclear interactions $\Delta\nu_m$, the total linewidth for the $m \leftrightarrow m-1$ NMR line is

$$\Delta\nu_t = (\Delta\nu_m^2 + \Delta\nu^2)^{1/2} \ . \tag{3}$$

We assume that the ESR and NMR line broadenings are linearly correlated according to

$$\frac{\bar{\nu}}{\Delta\nu} = p\frac{h}{\Delta h} \ , \tag{4}$$

where p is introduced as a correlation parameter whose magnitude ranges from 0 (completely uncorrelated broadening) to 1 (completely correlated broadening). The magnitude of the correlation parameter p is a measure of the relative size of the NMR line broadenings due to "microscopic" field inhomogeneities characterized by field variations within the shells of influence, and the "macroscopic" field inhomogeneities characterized by variations of the field from shell to shell across the sample. The case of $p = 1$ arises when the NMR field-inhomogeneity broadening is accounted for entirely by the variations from shell to shell ($\Delta\nu = \delta\bar{\nu}$). The other extreme case of $p = 0$ arises when the field is macroscopically homogeneous but varies only within the shells of influence ($\Delta\nu = \delta\nu$). Therefore, the term correlation may be used here to indicate the relative magnitude of the contributions of macroscopic and microscopic field inhomogeneities to the total NMR line broadening.

It is noted that there are one-to-one correspon-

dences between the present quantities and those pertinent to the correlated strain effect[4]; that is $h \leftrightarrow aD$, $\bar{\nu} \leftrightarrow b\bar{Q}$, $\Delta h \leftrightarrow a\Delta D$, $\delta\nu \leftrightarrow b\delta Q$, $\delta\bar{\nu} \leftrightarrow b\Delta\bar{Q}$, and $\Delta\nu \leftrightarrow b\Delta Q$. Therefore, by performing the same calculations as for the strain effect, we obtain the following expression for the $m \leftrightarrow m-1$ NMR line shape under DNP at the center of the ESR line broadened by external-magnetic-field inhomogeneities:

$$f_h(\nu) = I_h \nu \exp\left(\frac{-\nu^2}{2\Delta\nu_h^2}\right) , \tag{5a}$$

with

$$\Delta\nu_h^2 = \Delta\nu_m^2 + \Delta\nu^2\left[1 - \left(\frac{p\Delta h}{\Delta H_M}\right)^2\right] \tag{5b}$$

and

$$I_h = \frac{-pA_m\mathcal{E}_M e^{1/2}\Delta H_M^2\Delta\nu\Delta h}{(2\pi)^{1/2}[(\Delta\nu_m^2+\Delta\nu^2)\Delta H_M^2 - (p\Delta h\Delta\nu)^2]^{3/2}} . \tag{5c}$$

In the above expressions, $A_m \propto [I(I+1) - m(m-1)]$, ΔH_M is the half width between the maximum and miminum NMR enhancements due to the normal solid effect along the entire ESR line, and $\mathcal{E}_M$ is the value of the maximum NMR enhancement which is defined as the ratio of the first-derivative NMR intensity under the maximum DNP, I_M, to the first-derivative NMR intensity at thermal equilibrium I_0; the theoretical value of I_0 can be obtained from the thermal-equilibrium NMR line shape of

$$f_t(\nu) = \frac{A_m}{(2\pi)^{1/2}\Delta\nu_t}\exp\left(\frac{-\nu^2}{2\Delta\nu_t^2}\right) \tag{6}$$

as

$$I_0 = \frac{A_m e^{-1/2}}{(2\pi)^{1/2}\Delta\nu_t^2} . \tag{7}$$

Figure 2 illustrates the first-order NMR quadrupole structures characterized by Eq. (5) and the thermal-equilibrium NMR structures of Eq. (6) for the case of $I = \frac{5}{2}$. In plotting Eq. (5), the dependence of I_h on m through $\Delta\nu_m$ is assumed to be negiligibly small as compared to that through A_m. We also assumed that $(p\Delta h\Delta\nu)^2$ is vanishingly small.

Comparing Eqs. (5) and (6), one sees that the NMR absorption spectrum under DNP is proportional to the positive first derivative of a Gaussian function of width $\Delta\nu_h$; that is, the usual experimental first-derivative NMR spectrum under DNP would be proportional to the second derivative of a Gaussian line shape, with the central derivative intensity given by I_h, and the separation between the zero-derivative points given by $2\Delta\nu_h$ (see Fig. 3). Clearly, the intensity I_h vanishes for $p=0$ (the microscopic case) and

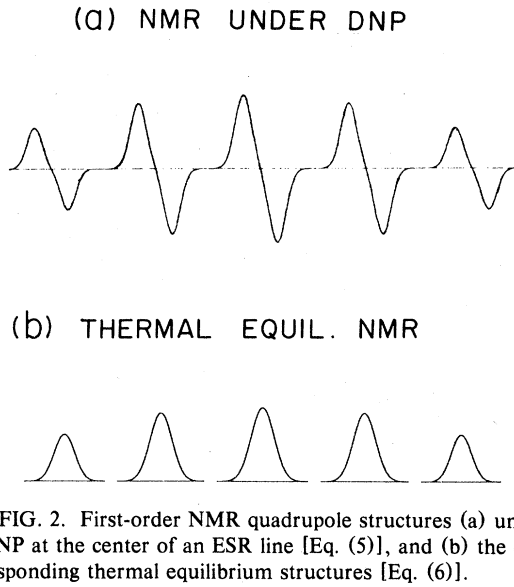

FIG. 2. First-order NMR quadrupole structures (a) under DNP at the center of an ESR line [Eq. (5)], and (b) the corresponding thermal equilibrium structures [Eq. (6)].

is maximum for $p=1$ (the macroscopic case). It should be pointed out that, unlike the strain[4] and c-axis-variation[6] effects, the NMR line shape of Eq. (5) occurs for all NMR lines under DNP from all ESR lines. One should remember that, in the cases of the strain and c-axis-variation effects, the unusual DNP phenomena vanish for the central $M = +\frac{1}{2} \leftrightarrow -\frac{1}{2}$ ESR line and for the central $m = +\frac{1}{2} \leftrightarrow -\frac{1}{2}$ NMR line. It was also true that in the latter cases, the low-frequency and high-frequency NMR satellite lines exhibited opposite phases with respect to the spectral base line, with an overall mirror symmetry for the entire NMR quadrupole structure. In the present case of inhomogeneous magnetic fields, all the NMR lines exhibit the same phase and there are no mirror symmetry properties for the NMR quadrupole structure.

As in the previous cases,[4,6] it is convenient to define the enhancement for the magnetic-field-inhomogeneity effect as the ratio $\mathcal{E}_h = |I_h/I_0|$. This can be obtained from Eqs. (5c) and (7) as

$$\mathcal{E}_h = \frac{(2.71)\, p\mathcal{E}_m\Delta h\Delta\nu\Delta H_M^2(\Delta\nu_m^2+\Delta\nu^2)}{[(\Delta\nu_m^2+\Delta\nu^2)\Delta H_M^2 - (p\Delta h\Delta\nu)^2]^{3/2}} . \tag{8}$$

All of the quantities in the above expression with the exception of the correlation parameter p can be obtained from ESR, NMR, and DNP experiments and thus the magnitude of p can be evaluated by comparing the experimental value of $\mathcal{E}_h$ with the value predicted by Eq. (8). This allows an experimental determination of the relative amount of macroscopic and microscopic field inhomogeneities.

Since quantities associated with thermal-equilibrium NMR spectra are often difficult to measure ac-

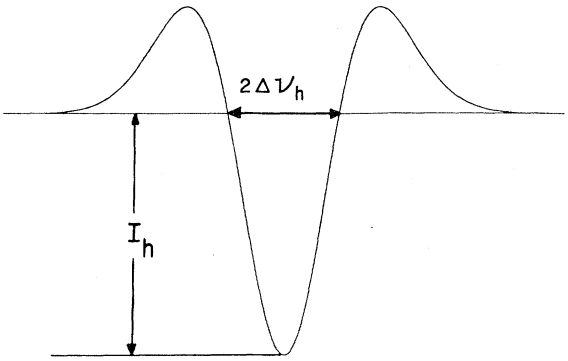

FIG. 3. First-derivative line shape of an NMR component line under DNP at the center of an ESR line [Eq. (5)].

curately owing to low signal-to-noise ratios, it is desirable to eliminate them as much as possible in the process of determining p. Thus we eliminate I_0, using the definitions of $\mathcal{E}_M$ and $\mathcal{E}_h$, and $\Delta\nu$ using Eq. (5b), yielding

$$\frac{I_h}{I_M} = \frac{(2.71)\Delta h\, p(\Delta\nu_h^2 - \Delta\nu_m^2)^{1/2}(\Delta\nu_h^2\Delta H_M^2 - p^2\Delta\nu_m^2\Delta h^2)}{\Delta\nu_h^3(\Delta H_M^2 - p^2\Delta h^2)^{3/2}} \tag{9}$$

Except for p, this expression contains only quantities that can be measured in ESR and DNP experiments, and all of the NMR quantities can be measured by the normal solid effect or the solid effect at the center of an ESR line broadened by the field-inhomogeneity effect.

III. EXPERIMENT AND DISCUSSION

The experimental equipment and procedures employed in the present work were similar to those used in the previous experiments for investigating the correlated strain[4] and c-axis-variation effects.[6] The crystal system investigated was a laser-quality single crystal of ruby containing a nominal 0.04 wt.% Cr^{3+} ion concentration.[9] All measurements were made with the external magnetic field directed parallel to the c axis of the ruby crystal at liquid-nitrogen temperature.

Our initial experiments were concerned with a qualitative investigation of the correlated magnetic-field-inhomogeneity effect. Using the central $(M = +\frac{1}{2} \leftrightarrow -\frac{1}{2})$ Cr^{3+} ESR transition, the NMR spectrum under DNP at the center of the ESR line was investigated in a region of the magnetic field known to contain a significant amount of inhomogeneity. The results are shown in Fig. 4(a). The important features of this spectrum are (i) that the central $(m = +\frac{1}{2} \leftrightarrow -\frac{1}{2})$ ^{27}Al NMR line does not vanish, and (ii) that all five NMR quadrupole lines have the same phase with respect to the base line. These are the two principal features which differentiate the field-inhomogeneity effect from the other sources, namely the strain and and c-axis-variation effects. It was necessary to ensure that we observed only the field-inhomogeneity effect in order that the analysis of our results was not hampered by the presence of these competing effects. Figure 4(b) shows the same spectrum recorded with the sample moved to the most homogeneous part of our magnetic fields (approximately 0.02 G within a radius of $\frac{1}{2}$ in. at the center of our magnetic pole faces). The effect is seen to vanish for all five NMR lines showing that the effect of Fig. 4(a) is indeed due to the field-inhomogeneity effect and not to the strain or c-axis-variation effects.

The second experimental phase consists of a series of quantitative investigations concentrating on the behavior of the central ^{27}Al NMR line under the influence of DNP from the central Cr^{3+} ESR line. The first step was the determination of the intrinsic width of the ESR line ΔH_0 in homogeneous fields. Then, after moving the sample to a region in the inhomogeneous fields where the ESR line was seen to be substantially broadened, the ESR linewidth was measured, yielding Δh based on Eq. (1). Maintaining the same sample position in the inhomogeneous fields, the DNP experiments were performed to measure the NMR enhancement as a function of magnetic field along the ESR line. The intensity of the NMR line at the point of maximum positive enhancement (I_M), and the width of the enhancement curve

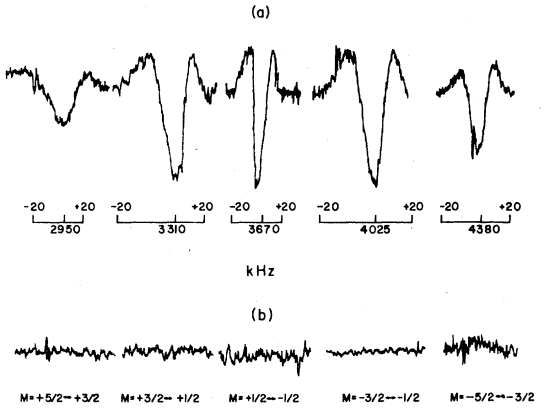

FIG. 4. ^{27}Al NMR quadrupole structures observed under DNP at the center of the $M = +\frac{1}{2} \leftrightarrow -\frac{1}{2}$ Cr^{3+} ESR line in ruby subjected to (a) inhomogeneous fields and (b) homogeneous fields.

TABLE I. Experimentally measured values for the Cr^{3+} ESR linewidth contributed by the external-magnetic-field inhomogeneities (Δh), the width of the NMR enhancement curve associated with the $M=+\frac{1}{2}\leftrightarrow-\frac{1}{2}$ Cr^{3+} ESR line (ΔH_M), the second moment of the $m=+\frac{1}{2}\leftrightarrow-\frac{1}{2}$ ^{27}Al NMR line in homogeneous fields ($\Delta\nu_m^2$), the half width (see Fig. 3) of the $m=+\frac{1}{2}\leftrightarrow-\frac{1}{2}$ ^{27}Al NMR line under DNP ($\Delta\nu_h$), the quantity $|I_h/I_M|$ as defined in Eq. (9), and the values of the correlation parameter p determined from Eq. (9).

Δh (G)	ΔH_M (G)	$\Delta\nu_m^2$ (kHz^2)	$\Delta\nu_h$ (kHz)	$\lvert I_h/I_M\rvert$	p
3.5	10.6	10.1	4.7	0.73	0.98
5.0	11.6	10.1	5.8	1.14	0.94
6.0	14.0	10.1	7.6	1.32	0.97

(ΔH_M) were measured. Then the magnetic field was adjusted to the center of the ESR line, and the NMR width ($\Delta\nu_h$) and intensity (I_h) under DNP at the center of the ESR line were determined. In this manner all of the quantities appearing in Eq. (9) were found, with the exception of the correlation parameter p. The procedure was repeated for different regions of increasingly inhomogeneous magnetic fields. The resultant experimental data are summarized in Table I.

Table I also displays the values of p determined by Eq. (8) using the various quantities listed in the table. For all three cases, the resultant p values turn out to be nearly unity, indicating that the inhomogeneous magnetic fields employed in the present experiments give rise to nearly perfect correlation between the ESR and NMR line broadenings. That is, the magnetic fields are associated with macroscopic inhomogeneities varying primarily from one shell of influence to another, and there are practically no magnetic-field variations within each shell. In our ruby sample with a Cr^{3+} ion concentration of 0.04 wt.%, the average size of the shells of influence, which is taken to be the average separation between two nearest-neighbor Cr^{3+} ions, is estimated to be roughly 140 Å. Thus the above results that the magnetic fields are nearly perfectly homogeneous within the dimension of 140 Å is expected from the field inhomogeneity (Δh) of several gauss across the sample in the present experiment.

IV. SUMMARY AND CONCLUSIONS

The phenomenological model previously developed for the correlated strain and c-axis-variation effects[4,6] has been extended to the case where the ESR and NMR line broadenings arise from inhomogeneities in the external magnetic fields. For the magnetic-field-inhomogeneity effect, all the $m\leftrightarrow m-1$ NMR component lines would exhibit positive first-derivative line shapes of the thermal equilibrium signals under DNP at the centers of all the $M\leftrightarrow M-1$ ESR component lines. This result contrasts with the strain[4] and c-axis-variation[6] effects in that the latter effects vanish, in first approximation, for the central $M=+\frac{1}{2}\leftrightarrow-\frac{1}{2}$ ESR and $m=+\frac{1}{2}\leftrightarrow-\frac{1}{2}$ NMR component lines. Our experimental results on a single crystal of ruby have shown that the external-magnetic-field inhomogeneities yield nearly perfectly correlated ESR and NMR inhomogeneous line broadening represented by the correlation parameter $p\simeq 1$; this can be taken as a direct verification of the phenomenological model.

With the conclusion of the present work, it can be stated that the phenomena of the correlated ESR and NMR inhomogeneous line-broadening effects have now been firmly established in single-crystalline solids. These phenomena, as revealed by DNP techniques, have been characterized in terms of a phenomenological model for the three important sources of inhomogeneous line broadening in single crystals, namely, the strain, c-axis-variation, and magnetic-field-inhomogeneity effects.

ACKNOWLEDGMENT

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[1]See, for example, C. D. Jeffries, *Dynamic Nuclear Orientation* (Interscience, New York, 1963); A. Abragam and M. Borghini, in *Progress in Low-Temperature Physics,* edited by C. J. Gorter (North-Holland, Amsterdam, 1964), Vol. 4.
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