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Investigations of Crystalline-Strain Effects on ESR and NMR by Dynamic Nuclear-Polarization Techniques*

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It is found that NMR structures under dynamic nuclear polarization (the solid effect) at the center of an electron-spin-resonance (ESR) line exhibit unusual line shapes resulting from crystalline-strain-induced variations in the ESR and NMR structure coupling constants in single crystals. Investigations of these line shapes enable one to determine directly the correlation between the effects of crystalline strains on the ESR centers and the surrounding nuclear spins in the crystals. This strain effect has been observed experimentally in a single crystal of ruby.

In this paper, we present a new method of studying crystalline-strain-induced variations in the electron-spin-resonance (ESR) and NMR structure coupling constants by means of dynamic nuclear polarization (DNP, the solid effect) at the center of an ESR line in single crystals. To illustrate the essential features involved in this method, we treat a single crystal containing (a) a concentrated nuclear-spin system which is perturbed by an axially symmetric quadrupole interaction, and (b) a dilute amount of paramagnetic ions which exhibit a fine-structure spectrum arising from an axially symmetric crystal-field interaction. It will be shown that the DNP method is capable of determining directly the correlation between the strain-induced variations in the fine-structure constant D of the ions and in the quadrupole coupling constant Q of the surrounding nuclei. To our knowledge, there is no other effective method available to investigate correlations of this type.

First, consider that the ESR lines of the paramagnetic ions are substantially inhomogeneously broadened by unresolved hyperfine interactions with the nearby nuclear spins. Thus, under the DNP produced by the solid effect, the NMR spectrum becomes positively enhanced for microwave pumping power applied at fields higher than the center of the ESR line, whereas it is negatively enhanced at lower fields; at the center of the ESR line the NMR signal is vanishing, according to the standard theory.[1] Thus the over-all enhancement is proportional to the negative of the first derivative of the ESR line.

As is well known, one of the important effects of crystalline strains on ESR and NMR spectra is to broaden their resonance lines. We consider that, for the crystal under consideration, the strain broadening of the ESR and NMR lines can be described solely by variations in D and Q values. Line broadenings arising from the variations in the symmetry axes of the quadrupole and fine-structure interactions associated with possible mosaic structures (c-axis variations) are taken to be vanishingly small. This situation is realized, for example, when the external magnetic field H is applied parallel to the symmetry axes of the ESR fine structure and NMR quadrupole interactions (assuming that the two axes coincide). For simplicity, we neglect the ESR and NMR line broadenings connected with inhomogeneities in H.

For further illustrative purposes the following model is employed: (i) The sample contains only three paramagnetic ions and is divided into three parts (1, 2, and 3), each part containing one ion. The D-value variations among these three ions are such that $D_1 < D_2 < D_3$, and the average of these values (namely, the whole sample average) denoted by $\tilde{D}$ is equal to D_2. The corresponding ESR fields H_1, H_2, and H_3 for a given ESR fine-structure line take the order of $H_1 < H_2 < H_3$, as shown in Fig. 1(a). (ii) There are three nuclear spins (a, b, and c) contained in each part of the sample contributing to the NMR signal. Thus the labeling Q_{2a}, for example, refers to the nuclear-quadrupole coupling constant for the spin a contained in part 2 of the sample, etc. (iii) Taking the "shell-of-influence" model[1] for the coupling between the paramagnetic ion and the surrounding nuclei, the nuclear spins in a given part of the sample are influenced only by the paramagnetic ion contained in this part during DNP processes.

There are several possibilities that can be considered for the variations in the nuclear Q values. However, the realistic situation is that the Q values of the nuclear spins are all slightly different, and in addition, the average Q values of the nuclear spins in different parts of the sample are also different. Then take the case $\tilde{Q}_1 > \tilde{Q}_2 > \tilde{Q}_3$, where $\tilde{Q}_1$, for example, refers to the average value of Q_{1a}, Q_{1b}, and Q_{1c} for part 1 of the sample, etc. The thermal-equilibrium NMR quadrupole structure for the various parts of the sample is displayed in the left-hand side of Fig. 1(b). It is noted in this figure that each quadrupole satellite component

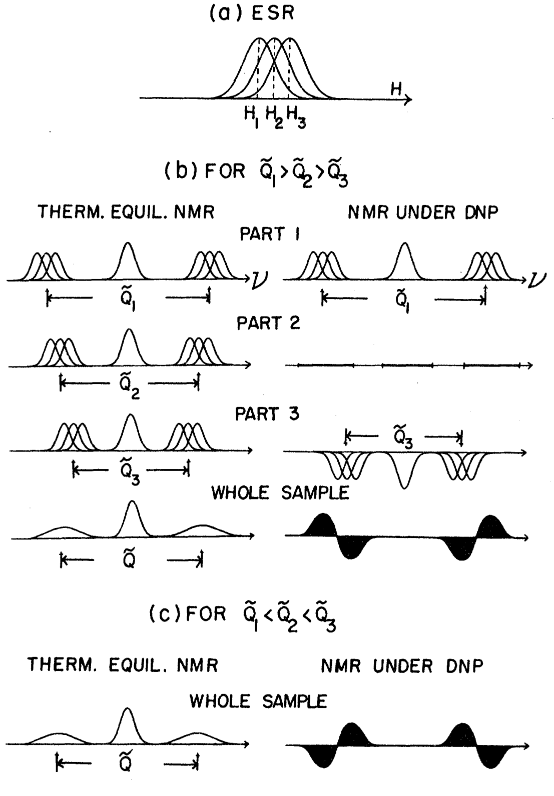

FIG. 1. Behavior of the NMR quadrupole structure ($I=\frac{5}{2}$) associated with the strain effect under DNP at the center of an ESR line.

from a given part of the sample consists of three lines, and their "center of gravity" is different for the different parts of the sample.

When microwave pumping power is applied at the center of the envelope of the three ESR lines of Fig. 1(a), it follows from the solid effect that the NMR signal from part 1 becomes positively enhanced, while that from part 3 becomes negatively enhanced; the NMR signal from part 2 is vanishing. These results are illustrated in the right-hand side of Fig. 1(b). The net effect of the indicated DNP experiment for the whole sample is to produce an NMR quadrupole structure quite different from that of the thermal-equilibrium signal [see the darkened spectrum in Fig. 1(b)]. Note that the central ($+\frac{1}{2} \leftrightarrow -\frac{1}{2}$) NMR line is vanishing, and the satellite lines are partly negatively enhanced and partly positively enhanced in such a manner that the low-frequency satellite line takes a shape which is a mirror image of the high-frequency satellite line. More important, the quadrupole spectrum is inverted with respect to the base line when the order of $\tilde{Q}_1$, $\tilde{Q}_2$, and $\tilde{Q}_3$ is reversed over the three parts of the sample; that is, $\tilde{Q}_1<\tilde{Q}_2<\tilde{Q}_3$. This is illustrated in Fig. 1(c).

The fact that the DNP at the center of the ESR envelope produces distinctly different NMR structures for the two cases—$\tilde{Q}_1>\tilde{Q}_2>\tilde{Q}_3$ and $\tilde{Q}_1<\tilde{Q}_2<\tilde{Q}_3$ (for a given order of $D_1<D_2<D_3$)—is very significant. The first case, $\tilde{Q}_1>\tilde{Q}_2>\tilde{Q}_3$, is the following: In part 3, where D_3 is taken to be larger than the whole sample average $\tilde{D}$, the average Q value of this part $\tilde{Q}_3$ is smaller than the whole sample average $\tilde{Q}$, under the assumption that $\tilde{Q}=\tilde{Q}_2$. On the other hand, in part 1 of the sample where D_1 is taken to be smaller than $\tilde{D}$, the average Q value of this part $\tilde{Q}_1$ is larger than $\tilde{Q}$. That is, the average deviation of the Q values for the nuclei surrounding a given paramagnetic ion is in the opposite direction to the deviation of the D value of the ion. The second case, $\tilde{Q}_1<\tilde{Q}_2<\tilde{Q}_3$, represents the fact that the deviation of the Q values for the nuclei surrounding a given paramagnetic ion is in the same direction as the deviation of the D value of the ion.

Thus the DNP method would enable one to find out the direct relationship between the D- and Q-value variations due to crystalline strains in different regions of the crystal. The conventional ESR or NMR method is capable of finding D- or Q-value variations, but only separately for the electron- or nuclear-spin system.[2] The DNP method illustrated here would not only reveal more details of these variations for each spin system, but also yield the correlation of the strain effects between the electron- and nuclear-spin systems.

The above results are derived from a simple crystal model. However, the same results are expected for real crystals containing electron- and nuclear-spin concentrations larger than those assumed in the simple model.

The strain effect has been observed experimentally in a single crystal of ruby (Al_2O_3: Cr^{3+}). Choosing the c axis of the crystal parallel to H, we investigated the detailed line shape of the Al^{27}-NMR quadrupole structure by saturating the centers of various Cr^{3+} ESR lines at a microwave frequency of 9.2 GHz, at liquid-nitrogen temperature.[3] A typical line shape observed in this experiment is shown in Fig. 2, in which we display the thermal-equilibrium absorption signal for comparison purposes. It is seen that the observed Al^{27}-NMR quadrupole structure under DNP is consistent with that predicted in Fig. 1 for the case of $\tilde{Q}_1<\tilde{Q}_2<\tilde{Q}_3$. This means that in the ruby crystal the average Q value of the Al^{27} nuclear spins surrounding a given Cr^{3+} ion is larger (smaller) than the whole sample average Q value, if the D value of this ion is larger (smaller) than the sample average D value.

It has previously been shown[4] that unusual NMR structures could also be produced under DNP at the center of an ESR line, if the ESR line is broadened by inhomogeneous magnetic fields and/or the c-axis variation effect. However, the NMR line shape due to the inhomogeneous magnetic fields is dif-

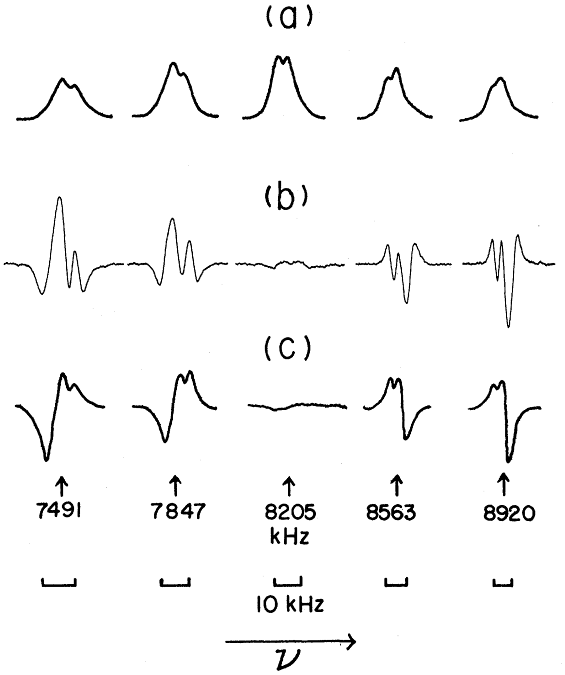

FIG. 2. (a) Thermal-equilibrium Al^{27}-NMR absorption spectrum in ruby; (b) the first-derivative NMR spectrum under DNP at the center of the $(+\frac{3}{2} \leftrightarrow +\frac{1}{2})$ Cr^{3+} ESR line; and (c) the absorption spectrum corresponding to the first-derivative spectrum of (b).

ferent from those produced by the strain effect in Fig. 2. In addition, the effect of inhomogeneous fields can be made negligibly small in practice.[5] It is also true that the c-axis variation effect can be eliminated or distinguished from the strain effect by investigating the angular dependence of the NMR structure under DNP. As previously reported,[6] DNP at the center of an ESR line which is inhomogeneously broadened by unresolved hyperfine interactions would produce a small NMR enhancement in the high-order calculations, resulting in NMR quadrupole structures different from that of the thermal-equilibrium signal. The unusual NMR line shape observed in the early DNP experiments on ruby in this laboratory was attributed to this effect.[7] However, we have found that the observed line shapes arose principally from the inhomogeneous magnetic field as well as the strain effects; if there was any contribution from the second-order effect, it must have been extremely small.

Thus, as has been demonstrated in Fig. 2 for the case of ruby, the experimental detection of the strain effect should not essentially be complicated by the other effects mentioned above, and would be very effective in a wide variety of single-crystalline solids.

The DNP method can be extended to crystals in which the electronic and nuclear interactions are not axially symmetric or in which the symmetry axes do not coincide. In principle the method can also be applied when the g tensor or the hyperfine-interaction tensor of a paramagnetic ion is sensitive to crystalline strains. The effects of crystalline strains on nuclear spins with $I \geqslant 1$ in cubic crystals might also be investigated by the indicated DNP method. We believe that quantitative treatment of experimental data obtained by the DNP method presented here would yield information very helpful to understanding the details of strain mechanisms influencing the behavior of the paramagnetic ions and nuclear spins in solids.

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[1] See, for example, C. D. Jeffries, *Dynamic Nuclear Orientation* (Interscience, New York, 1963).

[2] See, for example, R. F. Wenzel and Y. W. Kim, Phys. Rev. 140, A1592 (1965); M. H. Cohen and F. Reif, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5; B. R. McCart and R. G. Barnes, J. Chem. Phys. 48, 127 (1968).

[3] Under these conditions, the DNP effect associated with the electronic cross relaxation is not important—see V. A. Atsarkin, A. E. Mefed, and M. I. Rodak, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu 6, 942 (1967) [Sov. Phys. JETP Letters 6, 359 (1967)].

[4] H. H. Niebuhr, E. E. Hundt, and E. Brun, Phys. Rev. Letters 21, 1735 (1968); 22, 159(E) (1969); Helv. Phys. Acta 43, 777 (1970).

[5] We have found that a magnetic field homogeneity of approximately 30 mG was sufficient to eliminate this effect in ruby as well as in other crystals we have investigated.

[6] Sook Lee, Phys. Letters 26A, 572 (1968).

[7] Sook Lee, R. K. Jeck, and V. P. Jacobsmeyer, Phys. Rev. Letters 21, 515 (1968).