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Communication

On the analysis of broad Dysonian electron paramagnetic resonance spectra

Janhavi P. Joshi and S.V. Bhat*

Department of Physics, Indian Institute of Science, Bangalore 560012, India

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Abstract

We analyze the equation used for simulating the lineshapes of broad electron paramagnetic resonance spectra in conducting samples (i.e., broad Dysonian lineshapes) where it becomes necessary to include the effects of both clockwise and counterclockwise rotating components of the microwave magnetic field. Using symmetry arguments, we propose a modification to the equation. We show that the modified equation fits the experimental results better than the equation used in literature.

Keywords: EPR; Lineshape analysis; Dysonian

1. Introduction

The EPR spectrum in concentrated magnetic systems often consists of a single, broad, and featureless signal. The term broad here is employed to indicate that the linewidth (⩾100 mT) of the signal is of the same order of magnitude as the center field (∼330 mT for X band EPR). Then the informative parameters that one can extract from the spectrum are limited to the line position (or the g value), the linewidth, the lineshape, and their dependence on physical conditions such as temperature. The width of the signals puts a limit on the precision of the measurements of these parameters. Often, the only way to obtain these parameters from the broad and featureless spectrum is to fit an appropriate lineshape function to the signal. It is generally accepted that in powder samples of such magnetically concentrated systems exchange narrowing results in a signal which is Lorentzian in the most part except in the wings, where the shape is Gaussian [1] or exponential [2]. The Lorentzian region is understood to cover the magnetic field range $B = B_0 \pm a$, with $2a/\Delta B > 1$, where B_0 is the resonance field and ΔB is the linewidth. Since Gaussian wings are usually lost in the noise in the tail region the exchange narrowed signals can be fitted with Lorentzian shapes without much loss of accuracy. In majority of cases, symmetric signals are observed, the exchange narrowing leading to the averaging out of the anisotropies of other interactions.

In the case of conducting samples, however, due to the skin depth effects, one obtains an asymmetric signal of the Dysonian lineshape [3,4] which is a combination of the absorption and the dispersion components of a symmetric Lorentzian. An additional lineshape parameter viz. the A/B ratio i.e., the ratio of the amplitude of the left peak to that of the right peak of the derivative EPR signal or equivalently, α, the asymmetry parameter, which is the fraction of the dispersion added on to the absorption, is necessary to describe such an asymmetric signal. Accurate determination of the lineshape parameters for such an asymmetric broad line is conceivably more difficult.

When the signals are broad, one needs to take into account, an additional effect coming out of the nature of the microwave magnetic field. It is well known that the microwave field used in the standard EPR spectrometers is linearly polarized [5] and can be described by the equation

$$B_x = B_{x0} \cos \omega t, \tag{1}$$

where ω is the microwave frequency and B_{x0} is the amplitude. The subscript indicates that the alternating

* Corresponding author. Fax: +91-80-23602602.
E-mail address: svbhat@physics.iisc.ernet.in (S.V. Bhat).

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magnetic field is along the x-axis. This field can be split into two circularly polarized components, each of amplitude $B_1 = \frac{1}{2}B_{x0}$, one rotating clockwise and the other anticlockwise, given by equations:

$$B_R = B_1(\mathrm{i}\cos\omega t + \mathrm{j}\sin\omega t), \tag{2}$$

$$B_L = B_1(\mathrm{i}\cos\omega t - \mathrm{j}\sin\omega t). \tag{3}$$

For a given direction of the DC magnetic field, one component rotates in the same sense as the Larmor precession of the magnetic moment of the system under investigation and is responsible for the observed resonance and the other rotates in the opposite sense. Usually, the latter is neglected because for sufficiently narrow lines, that is for lines in which the linewidth is much smaller than the center field, the contribution of the effect of the counter rotating component becomes negligible. However, for broad signals it becomes necessary to include its effect. We note that with circularly polarized microwave field, if the 'g' factor is anisotropic and contains components of both positive and negative signs, then also EPR signals will occur on both sides of $B = 0$ [5].

The following equations which incorporate the effects of both the microwave components are used in literature [6] to describe broad EPR lines:

$$P = \left[\frac{\Delta B}{4(B - B_0)^2 + \Delta B^2} + \frac{\Delta B}{4(B + B_0)^2 + \Delta B^2}\right], \tag{4}$$

for broad symmetric Lorentzian spectra from powder samples and

$$P = \left[\frac{\Delta B + \alpha(B - B_0)}{4(B - B_0)^2 + \Delta B^2} + \frac{\Delta B + \alpha(B + B_0)}{4(B + B_0)^2 + \Delta B^2}\right], \tag{5}$$

for broad asymmetric Dysonian spectra from single crystal samples, where P is the power absorbed in the EPR experiment. In practice, field derivatives of $P(B)$ are recorded as EPR signals consequent to the magnetic field modulation used together with phase sensitive detection.

Using Eq. (5), in Figs. 1A and B we have simulated the curves and their derivatives, respectively. The dashed line represents the spectrum with a linewidth of 5 mT and the solid line represents the spectrum with a linewidth of 200 mT. From an examination of the curves in Fig. 1A, it can be seen that they are asymmetric about the zero field. Such an asymmetry about the zero field represents a physically unrealistic situation, since the response of the system to the changing static magnetic field is expected to be the same for the field increasing in

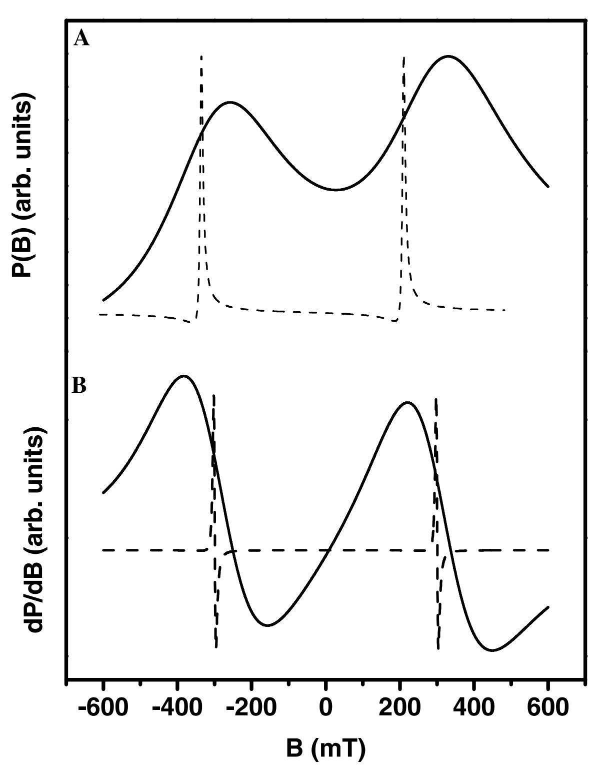

Fig. 1. (A) Dysonian lineshapes (Eq. (5)) plotted for positive and negative fields. The dashed line is simulated with a width of 5 mT and the solid line with a width of 200 mT. Note the asymmetry of the signals about $B = 0$. (B) The field derivatives of the signals.

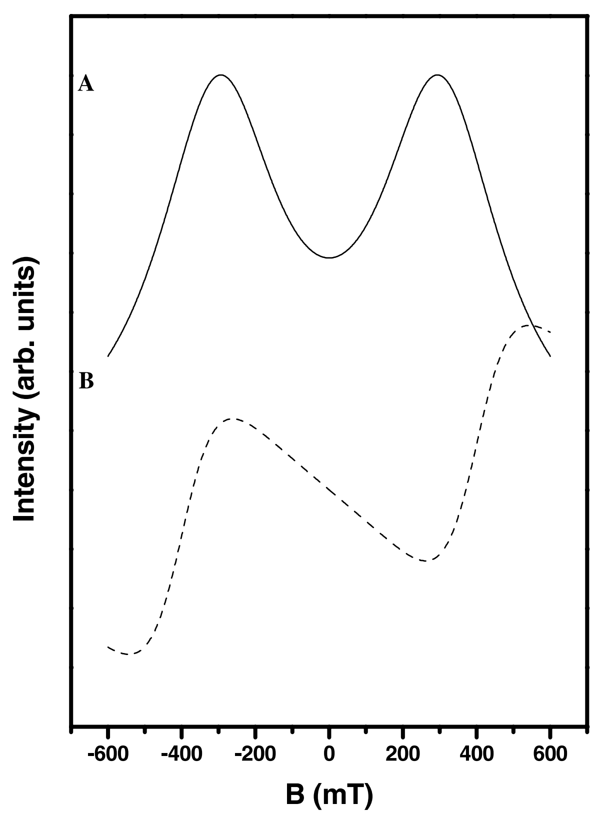

Fig. 2. The absorption (solid line) and the dispersion (dashed line) components of the broad signal in Fig. 1 are plotted separately. Note that while the absorption component is symmetric about $B = 0$ mT, the dispersion component is not.

magnitude from zero on either side of the zero field. To investigate the causes for the anomalous asymmetry observed, we have simulated the Lorentzian absorption and dispersion components of the broad signal of Fig. 1 separately in Figs. 2A and B, respectively. As can be seen from the figure, the Lorentzian absorption curve (Fig. 2A) is symmetric while the dispersion curve (Fig. 2B) is asymmetric about the zero field. Hence we conclude that the physically unrealistic asymmetry of Eq. (5), about the zero field is due to the asymmetry of the dispersion component of the Lorentzian.

To overcome this problem of asymmetry, we suggest a modification in Eq. (5). Since it is the dispersion component which causes the asymmetry about the zero field, we suggest that on the negative field side the dispersion component should be added with a reversed phase so that Eq. (5) now reads

$$P = \left[\frac{\Delta B + \alpha(B - B_0)}{4(B - B_0)^2 + \Delta B^2} + \frac{\Delta B - \alpha(B + B_0)}{4(B + B_0)^2 + \Delta B^2}\right]. \qquad (6)$$

We have plotted this lineshape in Fig. 3. As can be seen from the figure, the Dysonian signal, $P(B)$, now is symmetric around the zero field.

We have used this equation to fit some of the experimental signals obtained by us earlier [7]. The experimental signals along with the fits using Eqs. (5) (dotted line) and (6) (solid line) are shown in Fig. 4. As can be clearly seen from the figure, the fits obtained

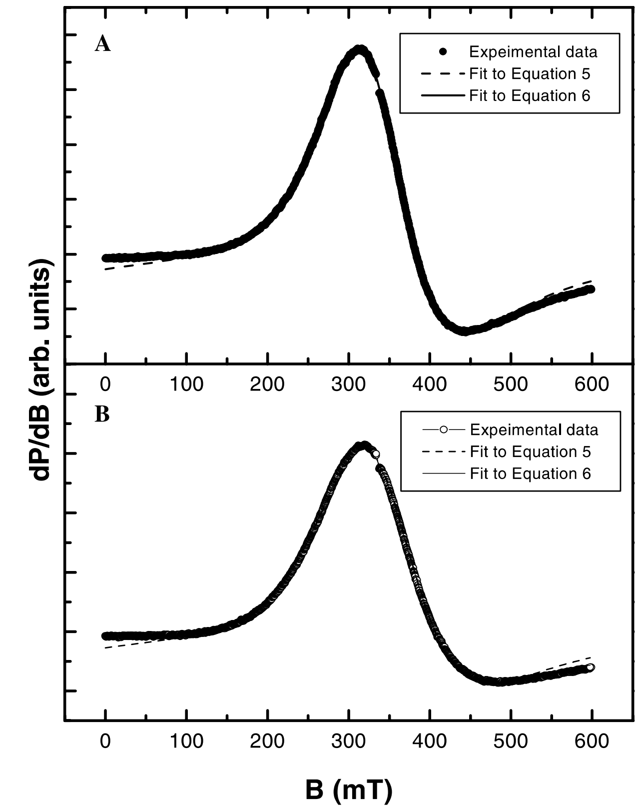

Fig. 4. EPR spectra from a single crystal of $Nd_{0.5}Ca_{0.5}MnO_3$ at (A) 238 K and (B) 225 K. Dashed line is the fit to dP/dB with $P(B)$ given by Eq. (5) and the solid line is the fit to dP/dB with $P(B)$ given by Eq. (6). The best fit parameters are: for 238 K, $\alpha = (0.92)$ 1.12, $\Delta B = (102.6\,\text{mT})$ 102.7 mT, and $B_0 = (342.1\,\text{mT})$ 337.5 mT with (Eq. (5)) Eq. (6) and for 225 K, $\alpha = (1.37)$ 1.89, $\Delta B = (117.5\,\text{mT})$ 118.9 mT, and $B_0 = (342.5\,\text{mT})$ 336.2 mT with (Eq. (5)) Eq. (6).

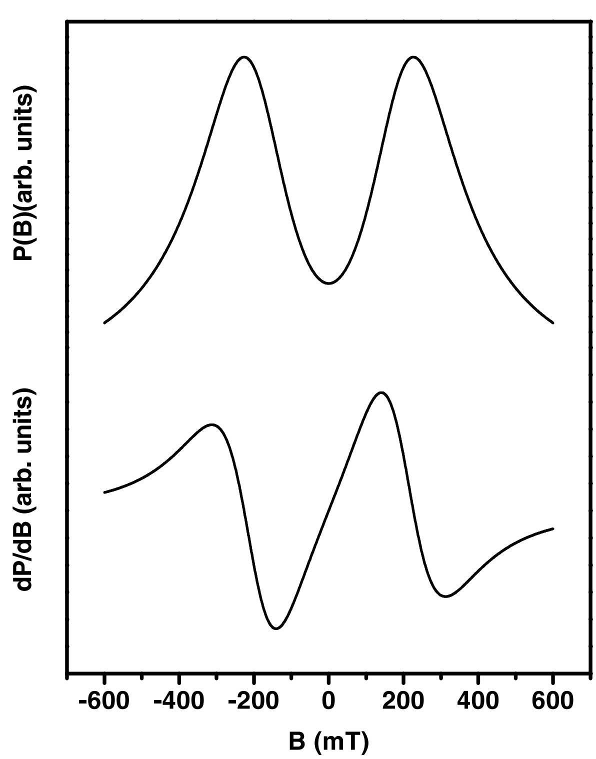

Fig. 3. Modified Dysonian lineshape (Eq. (6)) and its derivative. Note that $P(B)$ is symmetric around $B = 0$ mT.

using Eq. (6) are significantly better than those obtained using Eq. (5). A comparison of the best fit parameters given in the figure caption also shows that while the linewidth does not change appreciably with the equation used, both the asymmetry parameter α and the resonant field B_0 (and consequently the 'g' value) change significantly when Eq. (6) is used instead of Eq. (5).

In summary, we propose a modification to the lineshape function used for fitting broad Dysonian EPR signals and show that the modified equation results in better fits to the experimental spectra.

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