THE EFFECT OF A TEMPERATURE GRADIENT IN A SINGLE CRYSTAL ON E.P.R. LINE SHAPE AND WIDTH*

By Y. H. Ja†

Temperature is an important parameter in electron paramagnetic resonance experiments and studies at different temperatures can give a great deal of useful information about the investigated spin system and its interaction with its environment. Generally speaking, all of the parameters in the spin-Hamiltonian, such as the g factor, hyperfine interaction constants, etc., are independent of the temperature to a first-order approximation, but the line shape, line width, and spin–lattice relaxation time are quite sensitive to temperature changes. However, e.p.r. studies in many natural or synthetic crystals with very low concentrations of paramagnetic impurity-ions indicate that the line width ΔH and the line shape are virtually independent of the temperature T (provided T is not too low), while the crystal-field parameters in the spin-Hamiltonian, such as D and E, show a considerable variation with temperature. The former comes about because the line widths in such cases depend mainly on the mosaic structure (Shaltiel and Low 1961; Wenzel and Kim 1965) and the local distortions (mechanical or electrical strains) (Wenzel and Kim 1965) of the crystal lattice which are practically independent of the temperature. The latter is mainly due to the shrinkage or expansion of the crystal which changes the interactions between the paramagnetic ion and its neighbouring ions.

If, instead of working at a constant temperature as is normally done, we apply a temperature gradient in such a crystal, then in general the line width will be broadened and the line shape will be changed and distorted. These changes will be caused respectively by the temperature dependence of the spin-Hamiltonian parameters D and E etc. and by the different distributions of the spin population over the energy levels at different temperatures. We could term such (inhomogeneous) broadening "temperature broadening", somewhat analogous to the external electrical-field broadening (Mims and Gillen 1966) or other kinds of broadening. Because the overall e.p.r. spectrum of a crystal within a temperature range ΔT is normally much more complicated than that at a certain temperature T, the application of a temperature gradient through a crystal may only have limited use. In the following paragraphs we briefly investigate the effects of temperature gradient on the e.p.r. line width and shape and discuss some possible applications.

Theoretical Analysis

Suppose there is a uniform temperature gradient $\boldsymbol{G} = \Delta T/\Delta Z = (T_1 - T_2)/L$ along the Z axis of a small cylindrical single crystal. If the e.p.r. spectrum has axial

* Manuscript received 16 August 1971.

† School of Electrical Engineering, University of Sydney, Sydney, N.S.W.; present address: P.M.G. Research Laboratories, 59 Little Collins Street, Melbourne, Vic. 3000.

symmetry then the spin-Hamiltonian of the spectrum in a small volume element of the crystal can be expressed as

$$\mathscr{H} = \beta \boldsymbol{S} \cdot \boldsymbol{g}(T_n) \cdot \boldsymbol{H} + D(T_n)\{S_Z^2 - \tfrac{1}{3}S(S+1)\}, \tag{1}$$

where T_n is the temperature in the nth small volume element which can be considered constant. A lot of experimental e.p.r. data (Bleaney and Trenam 1954; Dvir and Low 1960; Ponton, Slade, and Ingham 1969; Ja 1970) indicate that the variation of the spectroscopic splitting factor g with temperature is much smaller than that of the axial field parameter D. Therefore, the variation of g can be neglected. Furthermore, we assume that

(1) The e.p.r. line width of the volume element is independent of the temperature T. (This is a good approximation for line broadening caused mainly by mosaic structure of strains.)

(2) The relation between the resonant magnetic field H_{0n} of the e.p.r. line in the volume element and the temperature T_n is linear. (We exclude for the present the possibility of a phase transition of the crystal lattice.) This is obviously a first-order approximation.

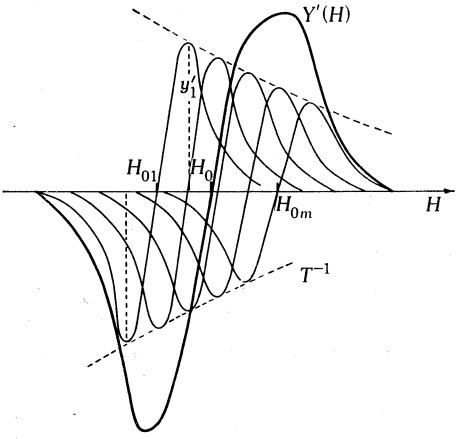

Fig. 1.—An asymmetric e.p.r. line resulting from the individual e.p.r. lines of volume elements of a crystal.

Because of the different temperature in every volume element of the crystal, the resonant magnetic field H_{0n} will also be different for different elements. From expression (1) and the foregoing assumption ($H_{0n} \propto T_n$) and taking into account the Boltzmann distribution of the spin populations in the energy levels at different temperatures, the features of the resultant e.p.r. line are shown in Figure 1.

If the e.p.r. line shape is taken to be Gaussian, the individual lines in Figure 1 have the form (Poole 1967)

$$y'(H) = y'_n \mathrm{e}^{\frac{1}{2}} \frac{H - H_{0n}}{\frac{1}{2}\Delta H_{\mathrm{pp}}} \exp\left\{-\tfrac{1}{2}\left(\frac{H - H_{0n}}{\frac{1}{2}\Delta H_{\mathrm{pp}}}\right)^2\right\}, \tag{2}$$

where y'_n and ΔH_{pp} are the amplitude and the line width between the maxima of

the first derivative of the e.p.r. line respectively. From (2) we easily obtain (Poole 1967)

$$y'(H) = \frac{4y_n(H-H_{0n})}{(\Delta H_{pp})^2} \exp\left\{-\tfrac{1}{2}\left(\frac{H-H_{0n}}{\tfrac{1}{2}\Delta H_{pp}}\right)^2\right\}, \tag{3}$$

where y_n is the amplitude of the e.p.r. line.

Consider the case of Fe^{3+} with a fictitious spin $S = 5/2$ and a considerably large zero-field splitting (Ja 1970). The overall energy difference between the six lowest energy levels in a magnetic field (usually $\leqslant$ 10–20 kG) will be about several hundred GHz and much smaller than kT when the temperature is far above the liquid helium temperature (4·2 K). The amplitude of the e.p.r. signal corresponding to the transition between two neighbouring energy levels, say 3 and 4, is

$$y_n = y_0(N_3-N_4)/\sum_{i=1}^{6} N_i, \tag{4}$$

which approximates under the above assumptions to

$$y_n \simeq y_0 h\nu/6kT, \tag{5}$$

where y_0 is a factor of proportionality. Substituting (5) into (3) yields

$$y'(H) = \frac{2h\nu y_0}{3kT_n} \frac{H-H_{0n}}{(\Delta H_{pp})^2} \exp\left\{-\tfrac{1}{2}\left(\frac{H-H_{0n}}{\tfrac{1}{2}\Delta H_{pp}}\right)^2\right\}. \tag{6}$$

The composite e.p.r. line is the arithmetic average of all the components:

$$Y'(H) = \frac{1}{m}\sum_{n=1}^{m} \frac{2h\nu y_0(H-H_{0n})}{3kT_n(\Delta H_{pp})^2} \exp\left\{-\tfrac{1}{2}\left(\frac{H-H_{0n}}{\tfrac{1}{2}\Delta H_{pp}}\right)^2\right\}. \tag{7}$$

Expression (7) is a good approximation to the real composite e.p.r. line when the index m of the sum is very large.

Calculated Results

The composite e.p.r. line $Y'(H)$ is easily calculated from equation (7) with a computer program, and results are shown in Figure 2 for two different cases given $T_1 = 290$ K, $T_2 = 90$ K, and the index $m = 100$:

Line A in Figure 2 has $H_{01} = 3900$ G, $H_{0m} = 3920$ G, and thus $\Delta H_0 = 20$ G. The resultant resonant field $H_0 = 3907$ G and $\Delta H_{pp} \simeq 21$ G.

Line B in Figure 2 has $H_{01} = 3895$ G, $H_{0m} = 3925$ G, and thus $\Delta H_0 = 30$ G. The resultant resonant field $H_0 = 3903$ G and $\Delta H_{pp} \simeq 29$ G.

The conspicuous features of these lines are:

(1) The line shape is asymmetric, the larger the ΔH_0 the more the asymmetry.

(2) The resultant resonant field H_0 is shifted from the average value of the resonant fields H_{01} and H_{0m} of the two outermost individual e.p.r. lines (see Fig. 1).

There are two extreme conditions:

$$\Delta H_0 \gg \Delta H_{pp}, \qquad \text{giving} \qquad \Delta H_{pp}\,|_{Y'} \simeq \Delta H_0,$$

in which the resultant e.p.r. line will be spread too wide to be detected; and

$$\Delta H_0 \ll \Delta H_{pp}, \qquad \text{giving} \qquad \Delta H_{pp}\,|_{Y'} \simeq \Delta H_{pp},$$

where the effect of $\Delta T/\Delta Z$ will be very small, the line shape will be almost symmetric, and the resonant field will be nearly unchanged.

If the width ΔH_{pp} of the e.p.r. line component is mainly due to spin–lattice interaction, it will be narrower when the temperature decreases. This will make the resultant line shape much more asymmetric than in the case considered here.

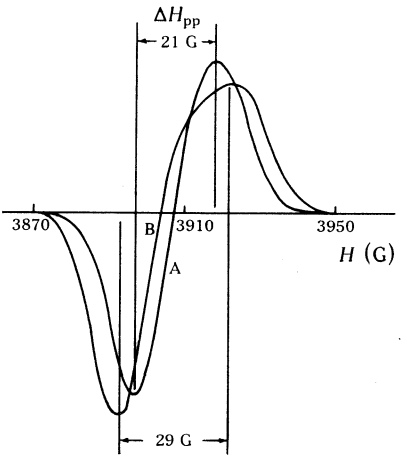

Fig. 2.—Composite e.p.r. lines for the two cases A and B as specified in the text. The line widths of the individual e.p.r. lines in both cases are 15 G. It is assumed that the resonant field H_{0n} increases when T increases.

Applications

(1) The present arrangement immediately gives an overall picture of an e.p.r. spectrum, mainly of line shape and width, in a certain temperature range ΔT. If the crystal lattice undergoes a phase transition at a temperature in the range ΔT, the e.p.r. line may split and the overall feature of the spectrum will substantially differ from that at a certain temperature T. This may offer a method of quickly detecting the phase transition of a crystal lattice over a particular temperature range.

(2) If the distribution of paramagnetic ions in a single crystal is inhomogeneous, e.g. if the density of impurity ions is different in different regions of the crystal or if the ions are concentrated in a surface of the crystal, then the e.p.r. line will change on rotation of the crystal by 180° about the vertical axis (Fig. 3). This method could be useful in investigating qualitatively the impurity distribution or the location of impurity ions. If the distribution of the paramagnetic ions is homogeneous while the temperature distribution along the crystal is not, investigation of the e.p.r. spectrum may give some information about the actual temperature distribution in the crystal along a certain direction.

(3) If some paramagnetic ions with high diffusion coefficients are artificially diffused from one end of the crystal to the other, the e.p.r. line position may slowly shift. This could give a means of investigating the diffusion of paramagnetic ions in a crystal.

(4) This method could also be helpful in identifying or distinguishing some unknown e.p.r. lines by comparing the results of the spectrum over a temperature range ΔT with that at a constant T, since the change in the width, shape, and position of an individual e.p.r. line depends upon

$$\mathrm{d}H_0/\mathrm{d}T \simeq (\mathrm{d}H_0/\mathrm{d}D)\mathrm{d}D/\mathrm{d}T\,, \tag{8}$$

in which $\mathrm{d}H_0/\mathrm{d}D$ may be very different for different transitions, D being the parameter defined in equation (1).

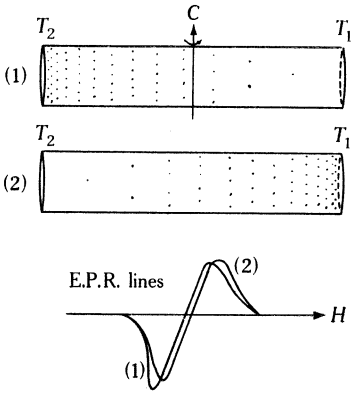

Fig. 3.—Change in the e.p.r. line when the specimen is rotated 180° about the axis C in a temperature gradient.

It can be concluded that in some cases the application of a temperature gradient in a single crystal offers an alternative method for investigation of the e.p.r. spectrum. Although quantitatively the results may not be as accurate as for the conventional method, some interesting additional information about the crystal may be obtained quite quickly.

Acknowledgments

The author is very much indebted to Professor R. E. Aitchison for a critical reading of the manuscript and for some useful suggestions. Most of this work has been carried out during the tenure of a Sydney University Postgraduate Research Studentship.

References

Bleaney, B., and Trenam, R. S. (1954).—*Proc. R. Soc.* A **223**, 1.
Dvir, M., and Low, W. (1960).—*Phys. Rev.* **119**, 1587.
Ja, Y. H. (1970).—*Aust. J. Phys.* **23**, 299.
Mims, W. B., and Gillen, R. (1966).—*Phys. Rev.* **148**, 438.
Ponton, R. G., Slade, E. F., and Ingham, D. J. E. (1969).—*J. Phys.* C **2**, 1146.
Poole, C. P., Jr. (1967).—"Electron Spin Resonance." p. 797. (Interscience: New York.)
Shaltiel, D., and Low, W. (1961).—*Phys. Rev.* **124**, 1062.
Wenzel, R. F., and Kim, Y. W. (1965).—*Phys. Rev.* **140**, A1592.