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Abstract. Low-frequency measurements for extracting hyperfine structure (HFS) parameters directly from the experimental ESR spectra of glasses are described. Glass of molar composition BaO–P$_2$O$_5$ with 0.2 wt% Mn$_2$O$_3$ was used. The spectra were recorded at room temperature in the UHF band at various frequencies (of 530 to 950 MHz). The HFS parameter A$_0$ was determined using the frequency dependence of the spectra.

1. Introduction

Quantitative information on short-range ordering in disordered solids can be obtained from ESR spectra only using computer simulation techniques [1,2]. The procedure for such information extraction (ESR spectrum parametrization) is an extremely time-consuming procedure, especially in the case of the high-order spin Hamiltonian matrix. Usually the high order of the matrix is concerned with the presence of both the electron spin and the nuclear spin of the paramagnetic ion. In this case the problem may be simplified using different approximate methods, for instance Bir's [3,4] method. At the same time there is an experimental way of simplifying the parametrization problem, namely ESR spectra measurement at very low microwave frequencies. Although such measurement has been made in a number of studies [5–9], this method has not been widespread. Probably this is because of the low sensitivity of the ESR spectrometer in this frequency band.

An attempt to develop the low-frequency measurement method for the extraction of the hyperfine structure (HFS) parameters directly from the experimental ESR spectra of glasses is presented in this paper. Since the Mn^{2+} ion is frequently used as a paramagnetic probe for structural studies and it has high values of electron and nuclear spins ($S = \frac{5}{2}$; $I = \frac{5}{2}$), this ion is the most suitable for such studies.

2. Samples and experimental results

Glass of molar composition BaO–P$_2$O$_5$ with 0.2 wt% Mn$_2$O$_3$ has been chosen for this study.

The measurements were carried out on a homodyne ESR spectrometer with 100 kHz modulation made by the present authors. The spectrometer has a coaxial tract with a bridge and bucking arm for smoothing the resonator absorption curve [10]. A loop gap like a quasi-stationary resonator was used as the resonant cell. The resonator frequency can be tuned by changing the capacitance. To compensate the effects concerned with the remnant
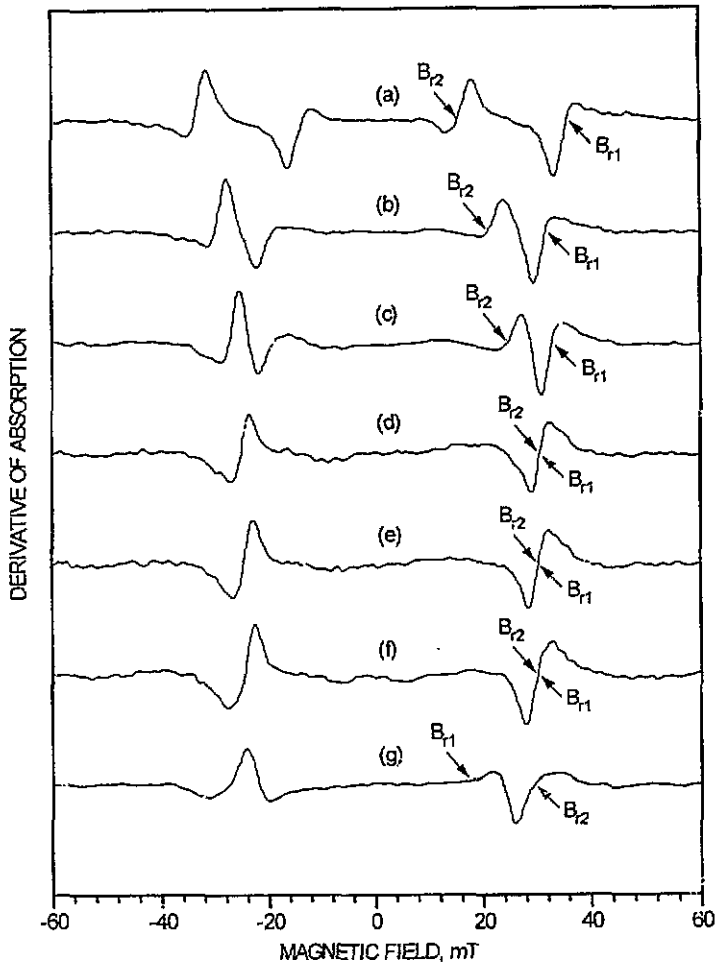
Figure 1. Experimental room-temperature ESR spectra of BaO–P_2O_5 glass doped with 0.2 wt% Mn_2O_3 for various frequencies: curve (a), 930 MHz; curve (b), 760 MHz; curve (c), 730 MHz; curve (d), 670 MHz; curve (e), 650 MHz; curve (f), 630 MHz; curve (g), 550 MHz.

magnet field a bipolar sweep from −60 to +60 mT was used. The value of the magnetic field was measured with a Hall sensor.

Spectra were recorded in the UHF band at various frequencies (530–950 MHz in steps of 20 MHz). Some of these spectra are shown in figure 1. It is seen that unlike the X- or Q-band ESR spectra, at a frequency $f = 930$ MHz the experimental ESR spectra of the Mn^{2+} ion contain only two relatively wide ($\delta B \approx 5$ mT) resonance lines. The lines become closer together with decreasing frequency. At frequency $f_0 \approx 650$ MHz these lines coincide and then diverge again. The lineshape at all frequencies has an asymmetry that is typical of anisotropic spin Hamiltonian parameters [1, 2]. Note that after the coincidence point the high-field spectral component smears out and disappears completely on further decreasing the frequency.

3. Theory

The ESR spectra of the Mn^{2+} ion in disordered solids are usually described by the rhombic spin Hamiltonian [11] of the form

$$H = g\beta B \cdot S + D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + AS \cdot I \tag{1}$$

where $g \approx g_e = 2.0023$ is the isotropic g-factor, β is the Bohr magneton, $S = \tfrac{5}{2}$ and $I = \tfrac{5}{2}$ are the electron and nuclear spins, respectively, D and E are the fine structure (FS) parameters and A is the HFS constant.

Usually the X- or Q-band spectra have been parametrized. In that case the condition $|D|$, $|E|$, $|A| \ll g\beta B$ holds. In the present case there are other conditions $|D|$, $|E| \gg g\beta B \approx A$. Since the energy level splitting caused by the ligand field is larger than those concerned with Zeeman and hyperfine interactions, to describe the experimental spectra the formalism of an effective spin [12] can be used. In zero external field there are three Kramers doublets, each characterized by effective parameters g and A.

According to the calculations in the strong ligand-field approach [1, 13], the spectral features of Mn^{2+} ESR spectra in disordered solids arise from the middle Kramers doublet. The effective g-factor value for the middle Kramers doublet to third order in perturbation theory is

$$g_{eff} = \tfrac{30}{7}[1 + \tfrac{4}{7}q(I_z^2 - I_y^2) + \tfrac{4}{49}(4p^2 + 15q^2)(I_y^2 + I_z^2)$$
$$- \tfrac{2}{49}(5p^2 + 4q^2)(I_y^2 - I_z^2)^2 - \tfrac{24}{343}(4p^2 + 17q^2)] \tag{2}$$

where

$$q = \frac{D - 3E}{D + E} \qquad p = \frac{\beta g_B B_r}{D + E} \qquad I_y = \sin\vartheta \sin\varphi \qquad I_z = \cos\vartheta.$$

The value of the parameter p can be easily evaluated. Having set the FS parameters according to [1, 2], i.e. $D/h \approx 6726$ MHz, $E/h \approx 1682$ MHz and $B_r = 30$ mT, one gets $p \approx 0.1$. The evaluation of the parameter q is somewhat complicated. If one uses the above FS parameters, one gets $q = 0$. However, these parameters have been determined with a precision of about 50 mT, and the parameter q may be evaluated as having the same value as the parameter p. Thus one can suppose that $q \approx p \approx 0.1$. In this case the anisotropy of the g-factor is small and one can assume that the experimental spectra in the first approach are described by the effective spin Hamiltonian

$$H = g\beta B \cdot \tilde{S} + A'\tilde{S} \cdot I \tag{3}$$

where $g = \tfrac{15}{7}g_e$ is the isotropic effective g-factor, β the Bohr magneton, $\tilde{S} = \tfrac{1}{2}$ the effective electron spin, $I = \tfrac{5}{2}$ the nuclear spin and $A' = \tfrac{15}{7}A$ is the isotropic effective HFS parameter.

The eigenvalues of the spin Hamiltonian (3) can be obtained in an analytical form because the energy matrix 12×12 may be blocked into 1×1 and five 2×2 submatrices. On the contrary, the eigenvalues of the spin Hamiltonian (1) can be obtained only using the numerical diagonalization procedure.

The results of the diagonalization of the matrix of spin Hamiltonian (1) with parameters $S = \tfrac{5}{2}$, $I = \tfrac{5}{2}$, $g = 2.0023$, $D/h = 6726$ MHz, $E/h = 1682$ MHz, $A/h = 240$ MHz, $\vartheta = 0$, 90 and $\varphi = 0.90$ for the middle Kramers doublet are shown in figure 2 (solid curves). The full circles in the same diagram represents the results of calculation for spin Hamiltonian (3) with the parameters $S = \tfrac{1}{2}$, $I = \tfrac{5}{2}$, $g = 4.28$ and $A/h = 240$ MHz.

The comparison of energy diagrams for the middle Kramers doublet (figure 2) shows that in both cases the energy diagrams almost coincide. Of course, in order to make the
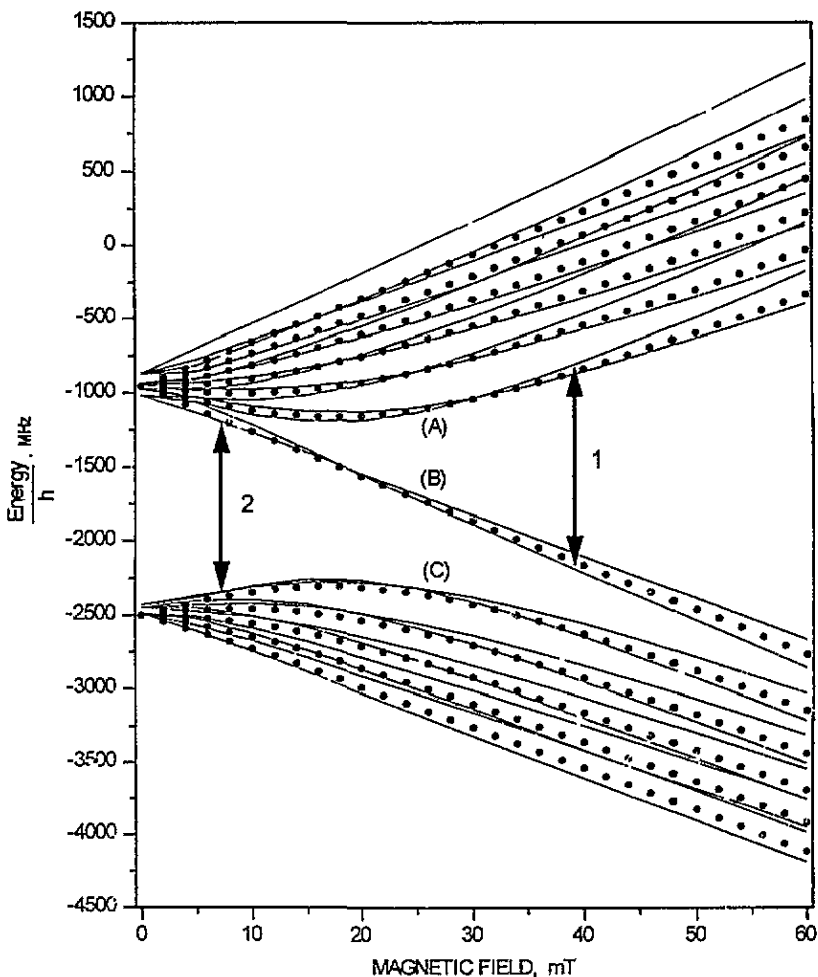
Figure 2. Energy diagrams for the middle Kramers doublet. The energy levels have been calculated using the spin Hamiltonian (1) with the parameters $S = \frac{5}{2}$, $I = \frac{5}{2}$, $g = 2.0023$, $D/h = 6726$ MHz, $E/h = 1682$ MHz, $A/h = 240$ MHz, $\vartheta = 0$, 90 and $\varphi = 0$, 90 (———) and the spin Hamiltonian (3) with the parameters $S = \frac{1}{2}$, $I = \frac{5}{2}$, $g = 4.28$ and $A/h = 240$ MHz (●). In order to make both the energy diagrams coincide, the constant 1600 MHz has been subtracted from each energy value of the diagram (see text).

energy diagrams coincide, it is necessary to take into account the constant displacement ε_0 of energy levels caused by the FS terms in the spin Hamiltonian (1). According to [2] the latter displacement of energy levels can be obtained to first order in perturbation theory:

$$\varepsilon_0 \approx -\frac{20}{21}(D - 3E). \tag{4}$$

Let us assume that $D/h = 6726$ MHz and $E/h = 1682$ MHz; one then obtains $\varepsilon_0/h = -1600$ MHz.

The analysis of the resonance conditions, using the spin Hamiltonian (3), gives two resonance magnetic fields B_{r1} and B_{r2} with frequency dependence corresponding to the experimental data. These resonance fields are concerned with transitions 1 and 2 between

the energy levels

$$\varepsilon_A = -a + \sqrt{36a^2 + b^2 - 8ab}$$
$$\varepsilon_B = 5a - b \tag{5}$$
$$\varepsilon_C = -a - \sqrt{36a^2 + b^2 - 8ab}$$

where $a = \frac{1}{4}hA'$ and $b = \frac{1}{2}g\beta B$.

The dependence of the resonance field on frequency is described by the following expressions:

$$B_{r1} = \frac{14}{15}\frac{hf}{g_e\beta}\frac{45A_0 + 7f}{15A_0 + 14f}$$
$$B_{r2} = \frac{14}{15}\frac{hf}{g_e\beta}\frac{45A_0 - 7f}{14f - 15A_0} \tag{6}$$

where f is the measurement frequency and $A_0 = A/h$ is the HFS constant (in megahertz).

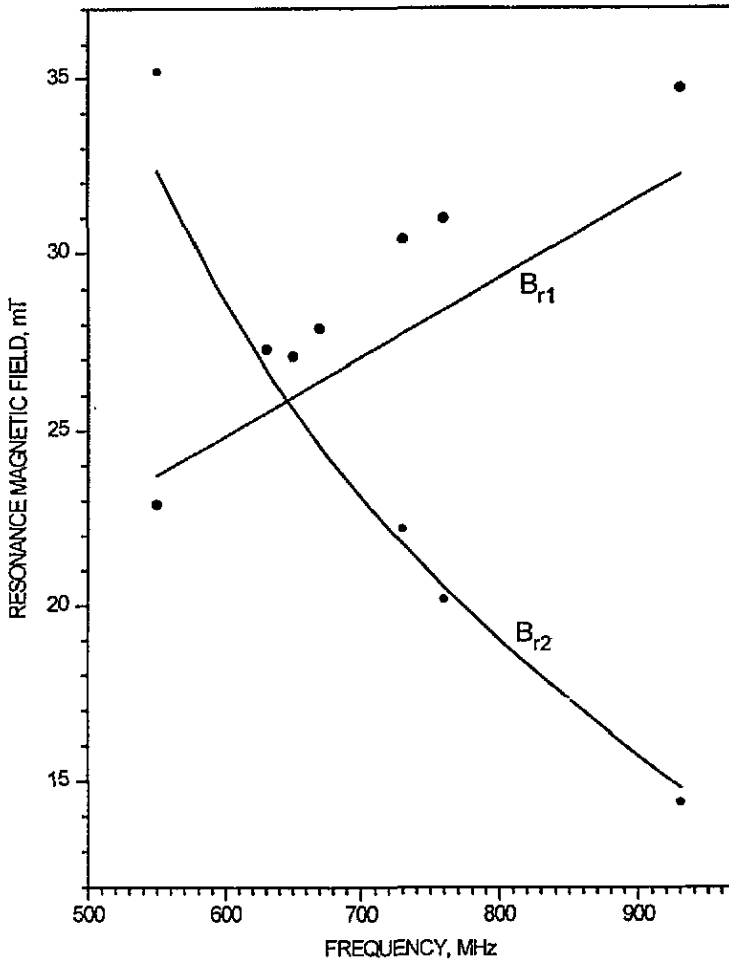The calculated positions of these resonance fields are also shown in figure 3.

Figure 3. The dependence of the resonance field on the measurement frequency f: ●, experimental data; ——, data calculated at $A_0 = 245$ MHz.

4. Discussion

Comparison of the line positions with the calculated resonance fields confirms the adequacy of the effective spin Hamiltonian (3) with respect to the experimental data and allows us to determine the value of the HFS constant A_0 as

$$A_0 = 245 \pm 20 \text{ MHz.}$$

The coincidence point (at frequency f_0) of resonance lines can also be used for an initial estimation of the HFS constant. Using equations (6), one obtains the relation between the constant A_0 and the frequency f_0:

$$A_0 = \frac{7}{15}\sqrt{\frac{2}{3}} f_0. \tag{7}$$

The frequency f_0 may be estimated from the spectra by visually determining the minimal half-width of resonance line. The half-width of the line can be determined relatively precisely.

The alternative method of estimating the constant A_0 is by using the expression

$$A_0 = \frac{7}{15}\sqrt{\frac{2}{3}}\sqrt{\frac{28f - 30g\beta\Delta B}{28f - 5g\beta\Delta B}} f \tag{8}$$

where $\Delta B = B_{r1} - B_{r2}$ and f is the measurement frequency.

The expression allows us to calculate the latter constant only from one spectrum that is measured at a frequency higher than f_0. However, it is somewhat more difficult to determine the line position than the linewidth because the line position is affected by the choice of baseline, especially in the presence of baseline drift. Therefore the precision of constant A_0 is less than determined by equation (7).

From figure 3, one can see a small difference (about 3 mT) between the position of the high-field component of experimental spectra and the calculated value of the magnetic resonance field. Probably this is due to anisotropy of the effective g-factor mentioned above. Indeed, disagreement between the energy diagrams (figure 2) has been observed at relatively high values of the magnetic field. Moreover, since for S ions the contact (isotropic) HF interaction predominates over the dipolar interaction [12], the observed lineshape can be explained only by assuming that the g-factor depends on the FS parameters D and E, the angles ϑ and φ between the applied magnetic field and the symmetry axis of the paramagnetic complex (see equation (2)). The disappearance of the high-field spectral component at low frequencies (after the coincidence point) is caused by the fulfilment of the resonance condition in a wide range of magnetic fields. Therefore this line is smeared out.

Study of the effective g-factor anisotropy using computer simulations of experimental lineshape will allow us to determine the value of the parameter q as well as to define more precisely the ratio of the FS parameters D and E. This study is in progress.

5. Conclusion

The spin Hamiltonian (3) must be regarded as the first approach for an expression that can describe the position of the resonance lines. The HFS parameter A_0 can be determined using the frequency dependence of spectra at low measurement frequencies. The initial evaluation of the HFS constant A_0 may be carried out by visual estimation of the frequency of the coincidence point.

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