

Stress effects on the ESR spectra of rare earths in polycrystalline thin films

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(Received 24 April 1985; revised manuscript received 4 November 1985)

A method for calculating the independent parameters in the spin-lattice Hamiltonian from ESR experiments performed in diamagnetic thin metallic films doped with rare-earth ions is given. One independent parameter is obtained as a function of the orientation of the film when the film is a single crystal. When the film is a polycrystal, one additional parameter is obtained. In the light of the present calculation, the existing data are analyzed as is the validity of previous interpretations. Finally, comments on the future of the technique are presented.

I. INTRODUCTION

The orbit-lattice interaction, which is responsible for the spin-lattice relaxation of magnetic ions in solids, is usually studied using stress techniques.¹ The stress shifts the ESR lines of magnetic impurities diluted in the solid, and, by fitting the spin-lattice Hamiltonian to the experimental results, the phenomenological parameters are obtained. A great deal of information has been gained through this kind of experiment for magnetic ions diluted in insulators. For the case of metals, however, the stresses necessary to shift the broad lines by half a linewidth are huge, and a modified technique has been used in the last decade.²⁻⁹ This new technique uses the fact that when a film is formed on a substrate which has a different thermal expansion coefficient, a change in temperature will induce a planar strain (i.e., isotropic in the interface plane) in the former. The nature of the film allows the strains to be very large within the elastic limit of the film (sometimes with values as high as some units percent),³ and the ESR spectra of the impurities is modified as in the previous method, so that the parameters of the orbit-lattice interaction can be evaluated.

One important difficulty inherent to the method is the growth of single crystalline films with a chosen orientation with respect to the substrate (i.e., with respect to the principal directions of the strain). One oriented sample is necessary for each parameter, and in the simplest case, for cubic metals where two second-order parameters are allowed by symmetry, at least two different orientations are necessary. Epitaxial growth has been used to obtain such samples, but this method has not always been successful.

In this Brief Report we present a calculation which gives a linear combination of the spin-lattice parameters when the film is a polycrystal, whether oriented at random or with preferential orientation. This result can be helpful for the experimentalists, because it allows one to obtain the second-order parameters with samples that are not necessarily single crystals (e.g., one polycrystal and one single crystal, or two polycrystals with different, but known preferred orientations), and at the same time clarifies the interpretation of already published data.

II. CALCULATION

The effect of the strain on the ground state of the magnetic ion is described with the phenomenological spin-lattice

Hamiltonian \hat{H}_{SL} . This operator is a linear function of the components of the strain tensor ϵ_{ij} , and must be invariant under the operations of the point group G of the ion. The \hat{H}_{SL} is a function of the magnetic field \mathbf{H} and of the effective spin operator \tilde{S} , so that $2 \times |\tilde{S}| + 1$ gives the degeneracy of the magnetic ion's ground state. For Kramers' doublets, $|\tilde{S}| = \frac{1}{2}$ and we write

$$\hat{H}_{SL} = \mu_B \sum_{i,\alpha,\zeta,\zeta'} g_i^{(\zeta,\zeta')} \epsilon_{i\alpha}^{\zeta,\zeta'} O_{i\alpha}^{\zeta,\zeta'}(\tilde{S}, \mathbf{H}), \quad (1)$$

where $\epsilon_{i\alpha}^{\zeta,\zeta'}$ are the normal strains, which are linear combinations of the six components of the strain tensor that transform like the α component of the i th irreducible representation of the group G , and the $O_{i\alpha}^{\zeta,\zeta'}(\tilde{S}, \mathbf{H})$ are spin-and-field operators, transforming likewise. The $g_i^{(\zeta,\zeta')}$ are the spin-lattice coefficients to be obtained from the experiments. The indexes ζ and ζ' in Eq. (1) are necessary when there is more than one normal strain or spin-and-field operator allowed by the transformation rules. The $\epsilon_{i\alpha}^{\zeta,\zeta'}$ are tabulated in Ref. 5 for the cubic point groups, and μ_B is the Bohr magneton.

Two different right-handed Cartesian coordinate frames are used in this work. One is the crystal frame, with axes x , y , and z attached to the crystal. For a cubic crystal, we take x , y , and z along the [100], [010], and [001] cubic axes, respectively. The other is the laboratory frame, with the z' axis perpendicular to the film-substrate interface, and the x' and y' axes in the plane of the interface. There is a preferential direction for the x' and y' axes, as discussed below.

To proceed with the calculation, the following working hypotheses are necessary:

(a) The film is firmly attached to the substrate at the interface plane. Changes in temperature do not affect the strength of the bond.

(b) Both the film and the substrate have isotropic thermal expansion coefficients $\alpha_{\text{film}}(T)$ and $\alpha_{\text{substrate}}(T)$ (i.e., they are cubic crystals or amorphous materials) and the film strain ϵ'_{xx} and ϵ'_{yy} are given at T_M by

$$\epsilon'_{xx} = \epsilon'_{yy} = \int_{T_M}^{T_D} [\alpha_{\text{film}}(T) - \alpha_{\text{substrate}}(T)] dT, \quad (2)$$

where T_D is the deposition temperature.

(c) Shear strains are null in the laboratory frame.

(d) The surface of the film is free from stresses.

(e) The strains across the film are homogeneous.

With the hypotheses above we calculate the strain tensor

in the laboratory frame: Only its diagonal components are different from zero in this frame. The stress tensor $\bar{\sigma}$ in the substrate frame can have three nonzero components, depending on the orientation of the crystal with respect to the substrate. They are σ'_{xx} , σ'_{yy} , and σ'_{xy} . As any rotation around the z' axis leaves $\bar{\epsilon}$ unchanged, we can rotate

$$\rho = \left(\frac{1}{2}\right) \arctan[\sigma'_{xy}/(\sigma'_{xx} + \sigma'_{yy})] ,$$

which makes the stress tensor diagonal too. These directions of x' and y' on the interface were chosen as principal axes for the laboratory frame. Both the strain and the stress tensors are therefore diagonal in this laboratory frame.

The normal stresses $\sigma'_{i\alpha}$ are defined in the same way as the normal strains, and with the same normalization.⁵ This simplifies the transformation of operators, allowing the use of tables published for the point groups.¹⁰ Three Euler's angle rotations: ψ around the z' axis, θ around the y axis after the first rotation, and ϕ around the new z , are necessary to transform the stress tensor to the crystal frame, where the elastic compliances S_{ij} are known. The normal stresses in the crystal frame, multiplied by the elastic compliance matrix, give the normal strains:

$$\begin{aligned} \epsilon_{1g} &= (S_{11} + 2S_{12})\sigma_{1g} , \\ \epsilon_{3gi} &= (S_{11} - S_{12})\sigma_{3gi} \quad (i = \theta, \eta) , \\ \epsilon_{5gj} &= S_{44}\sigma_{5gj} \quad (j = \kappa, \lambda, \mu) . \end{aligned} \quad (3)$$

The inverse rotation of Eq. (4) to the laboratory frame gives

$$\epsilon'_{3g\theta} = -\left(\frac{1}{4}\right)(\sigma'_{xx} + \sigma'_{yy}) \times [F_3(\theta, \phi)(S_{11} - S_{12}) + F_5(\theta, \phi)S_{44}] , \quad (4a)$$

$$\epsilon'_{1g} = (S_{11} + 2S_{12})(\sigma'_{xx} + \sigma'_{yy}) , \quad (4b)$$

with

$$F_3(\theta, \phi) = \left(\frac{1}{2}\right)[(3 \cos^2\theta - 1)^2 + 3 \sin^4\theta \cos^2(2\phi)] , \quad (5a)$$

$$F_5(\theta, \phi) = \left(\frac{3}{2}\right)[\sin^2(2\theta) + \sin^4\theta \sin^2(2\phi)] . \quad (5b)$$

Combining Eqs. (4a) and (4b), the relationship between the three components of the strain tensor in the laboratory frame is

$$\begin{aligned} \gamma(\theta, \phi) &= \frac{2\epsilon'_{zz}}{\epsilon'_{xx} + \epsilon'_{yy}} \\ &= \frac{4(S_{11} + 2S_{12}) - 2F_3(S_{11} - S_{12}) - 2F_5S_{44}}{4(S_{11} + 2S_{12}) + F_3(S_{11} - S_{12}) + F_5S_{44}} , \end{aligned} \quad (6)$$

with F_3 and F_5 defined in Eq. (5). Thus the entire set of normal strains is therefore known as a function of ϵ'_{xx} or ϵ'_{yy} .

To calculate the shift caused by the strain in the energy separation of the doublet, we diagonalize the spin-lattice Hamiltonian. Its eigenvalues are

$$E_{\pm 1/2} = \pm \mu_B H \frac{\epsilon'_{xx}(\gamma - 1)}{4} (g_{3g}F_3 + g_{5g}F_5) \frac{1}{2} (3 \cos^2\theta - 1) , \quad (7)$$

and we write the g shift for the ESR line, as

$$\Delta g = \frac{\epsilon'_{xx}(\gamma - 1)}{2} (g_{3g}F_3 + g_{5g}F_5) , \quad (8)$$

which corresponds to the maximum energy difference in Eq. (7). The effect of the hydrostatic strain in Eqs. (7) and (8), that is, the g_{1g} parameter, has not been taken into consideration since it cannot be observed in any experiment.

Let us consider our film as composed of many small randomly oriented crystallites. The contribution to the angular variation of the g value of each crystallite will depend on the crystallite orientation as given by Eq. (8). Assuming that the g shift for each crystallite is independent of its neighbors, the measured g shift will be the average of Eq. (8) over all orientations. The result is

$$\langle \Delta g \rangle / \epsilon'_{xx} = (g_{3g}/2) \langle (\gamma - 1) F_3 \rangle + (g_{5g}/2) \langle (\gamma - 1) F_5 \rangle , \quad (9)$$

where $\langle \rangle$ indicates the average over all the orientations in space.

There are several methods that can be used to calculate the mean values on the right side of Eq. (9).¹¹ As there is always a large number of crystallites in a sample, a continuous probability frequency function (PFF) can be assumed for the orientations. If we take a randomly oriented sample, the PFF for any function $F(\theta, \phi)$ is

$$W(F) = \frac{1}{4\pi} \int_0^{2\pi} d\phi' \int_0^\pi \delta(F(\theta, \phi) - F(\theta', \phi')) \sin\theta' d\theta' , \quad (10)$$

where δ is the Dirac delta function. Applying Eq. (10) to $F = (\gamma - 1)F_3$ and to $F = (\gamma - 1)F_5$, the corresponding PFF's are obtained, and from them we can get the corresponding mean values.

This simple analytical calculation, however, cannot be applied when the sample has preferred orientations. In that case different orientations have different weights which are sample dependent. The weights can be obtained using a diagram of poles¹² which is obtained through x-ray experiments. The easiest way to obtain the PFF's for $(\gamma - 1)F_3$ and $(\gamma - 1)F_5$ is to perform the calculation numerically.¹³ This has been done in this work and it allows one to get the PFF's and the mean values in every case.

The PFF's of $(\gamma - 1)F_3$ and $(\gamma - 1)F_5$ are dependent on the elastic compliances of the metal forming the film [see Eq. (7)], as are the mean values, which are tabulated in Table I for Ag, Al, and Au. To show the relative importance of the different values of the variables on the statistics, the PFF's for $(\gamma - 1)F_3$ and $(\gamma - 1)F_5$ obtained from the numerical calculation are shown in Fig. 1 for a random sample of silver. The integration necessary to calculate the mean values was also done numerically.

To include anisotropic crystals or substrates in the calculation, the corresponding anisotropy must be included in the induced strains ϵ'_{xx} and ϵ'_{yy} in Eq. (2); Eq. (2) to Eq. (9) remain valid.

TABLE I. Mean values for the angular dependence of the Γ_3 and Γ_5 modes in cubic thin films.

Sample	$\langle (\gamma - 1)F_3 \rangle$	$\langle (\gamma - 1)F_5 \rangle$
Al	1.126	1.235
Ag	1.203	1.248
Au	1.190	1.368

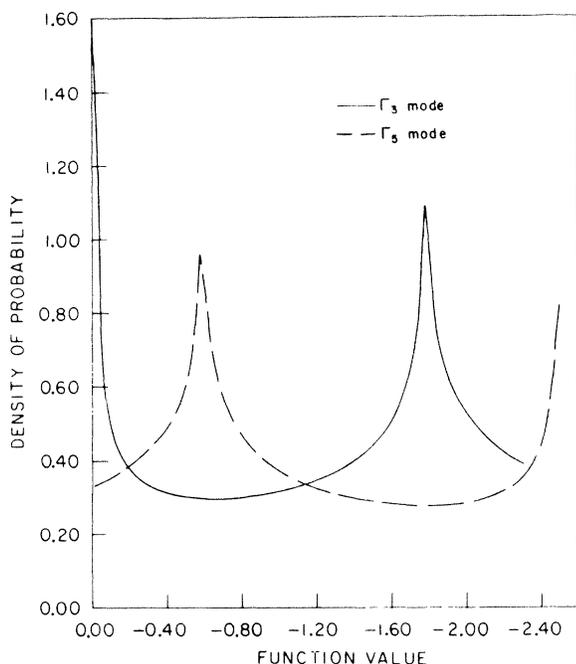


FIG. 1. Probability frequency functions of $(\gamma-1)F_3$ and $(\gamma-1)F_5$ for silver.

III. RESULTS AND ANALYSIS

To show the usefulness of the present calculation we shall apply it to existing data and show how it helps to understand the physics relevant to the experiment.

Each experiment is made in a particular film and substrate. As the stress is planar, when the magnetic field is rotated in a plane perpendicular to the film, the angular dependence of the ESR line is given by

$$g = g_0 + \Delta g \frac{1}{2} (3 \cos^2 \theta - 1) \quad (11)$$

independent of the film structure. In order to relate Δg in Eq. (11) to a particular phenomenological or microscopic parameter, it is necessary to introduce the structure of the film in the calculation. This requires knowledge of that structure, which can be obtained through x-ray experiments. This is taken into account in the analysis below for all the

films where it was reported.

Table II contains a summary of the experimental data, together with some results of the calculation. The experimental Δg 's have been divided by the strain values as estimated from Eq. (2), assuming that there are no sliding effects at the interfaces. This assumption is very reasonable when many different samples have been reported, as in Ref. 7. In this case, the largest $\Delta g/\epsilon'_{xx}$ reported corresponds with the smallest sliding of the film [as ϵ'_{xx} is always calculated using Eq. (2)]. The $\Delta g/\epsilon'_{xx}$ value given in Table II is the largest of the reported data. In other cases, the only reported values are presented in this table. When the films were oriented, as is the case of Au:Er and Ag:Er samples, the use of Eq. (8), with the corresponding values for θ and ϕ , gave us the spin-lattice Hamiltonian parameters shown in Table II. If both g_3 and g_5 were obtained from the experiments, the $\langle \Delta g \rangle / \epsilon'_{xx}$ could be calculated from these data and Eq. (10). This is the case for Au:Er, Ag:Er, Au:Yb, and Ag:Dy, where the predicted values are listed in the last column of Table II.

There are only two cases (Ag:Er and Ag:Dy) where there are both calculated and experimental data for the randomly oriented polycrystalline samples. A fairly good agreement is found for Ag:Er, but for Ag:Dy the experimental number is about 40% bigger than the calculated one. As the experiment reported in Ref. 8 does not contain any reference to the experimental (x-ray) film structure, the author is tempted to assume that the film was preferentially [111] oriented, which is also supported by the fact that the reported value is 20% smaller than the experimental $\Delta g_5/\epsilon'_{xx}$ (see Table II, and also Ref. 5). Large sliding effects could also have been present in this case.

The full strength of the calculation is used for Al films. It is especially difficult to grow Al films with the [100] axis perpendicular to the substrate; most samples grow with [111] orientation. The $\Delta g/\epsilon'_{xx}$ values are obtained from experiments on the latter samples and, using Eq. (8), one is able to obtain the g_5 parameter. Cooling down the substrates to temperatures around that of liquid N_2 , it is possible to grow randomly oriented samples. Experiments done on these last samples give one the $\langle \Delta g \rangle / \epsilon'_{xx}$ values, which, together with the g_5 parameter and the use of Eq. (9), give one the g_3 parameter. The obtained parameters are listed in Table II.

Equation (9) was employed directly for Au films. The values reported in this case correspond to oriented films,

TABLE II. Comparison between calculated values and existing experimental data. All the nonreferenced data were obtained through the calculation developed in the text.

Film	Experimental			Theory		
	g_{3g}	g_{5g}	$\Delta g_3/\epsilon'_{xx}$	$\Delta g_5/\epsilon'_{xx}$	$\langle \Delta g \rangle / \epsilon'_{xx}$ (poly.)	
Al:Dy	29.6	70.2 ^a	...	170.0 ^a	-120.0 ^a	...
Al:Er	133.5	-218.0 ^a	...	530.0 ^a	119.0 ^a	...
Ag:Dy	6.1 ^b	83.8 ^b	-15.3 ^b	-195.6 ^b	-153.3 ^c	-111.9
Ag:Er	-1.73 ^d	-24.3 ^d	4.35 ^d	56.8 ^d	33.3 ^c	32.4
Au:Er	-10.6 ^d	20.0 ^d	28.5 ^d	-51.9 ^d	...	-14.7
Au:Yb	-0.64 ^e	15.5 ^e	1.74 ^e	-40.2 ^e	...	-20.4

^aReference 9.

^bReference 5.

^cReference 8.

^dReference 7.

^eReference 6.

both with the [100] and [111] axes perpendicular to the interface, and the present calculation predicts the values of $\langle \Delta g \rangle / \epsilon'_{xx}$ which would be expected from experiments performed in randomly oriented Au:Er and Au:Yb thin films.

The author believes that the present calculation shows the correct manner to use the existing experimental results to predict the values for different film structures, and that complete knowledge of the film structure is necessary to obtain valid conclusions.

The author is not optimistic about the future use of thin films as strain gauges as the authors of Ref. 2 are, for there is a great experimental difficulty to know the actual value of

ϵ'_{xx} and to avoid sliding of the film relative to the substrate; nevertheless, we have found some good agreement between predictions and experiments.

ACKNOWLEDGMENTS

The author wishes to acknowledge Professor M. Foglio and Professor Alvin Kiel for critically reading the manuscript. This work was partially supported by Fundação de Amparo e Pesquisa do Estado de São Paulo (FAPESP) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Brazil.

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¹³The calculation is based on calculating a normalized histogram of the functions for the whole range of values, for a large number of points. The program can be used for any function of the angles, and a copy shall be sent on request.