

Investigation of the residual linewidth of Ag:Er dilute alloys

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The reflection-electron-spin-resonance residual linewidth for varying concentrations (125 to 2000 atomic ppm) of silver doped with erbium has been investigated at 9.0 and 1.7 GHz. The frequency-independent (homogeneous) broadening scales linearly with concentration and can be attributed to dipole-dipole interactions between the impurity spins. The frequency-dependent (inhomogeneous) broadening, also linear in concentration, is attributed to an increase in Kohn-Vosko oscillations of the charge density.

I. INTRODUCTION

There have been experimental reports^{1,2} on the concentration dependence of the residual linewidth in reflection-electron spin resonance (RESR) of dilute localized moments in metals at x-band (≈ 9 -GHz) frequencies. There has been, as yet, no attempt to determine the origin of the residual ($T \rightarrow 0$) concentration-dependent broadening of the RESR spectra. Systematic analysis requires the determination of the relative contributions of homogeneous and inhomogeneous broadening. The separation of the two types of broadening requires data to be taken at a minimum of two well-separated frequencies. Inhomogeneous broadening scales with frequency (as frequency increases, the linewidth increases linearly), whereas the homogeneous broadening should be independent of frequency.

We have recently completed construction of a 1.7-GHz RESR spectrometer that, in connection with a 9.0-GHz RESR spectrometer, allows us to separate the two types of broadening for Ag:Er dilute alloys. This is possible because of the large frequency ratio ($9.0/1.7 = 5.3$) of the two spectrometers. The experimental techniques utilized in sample preparation, as well as the RESR results, are discussed in Sec. II. We present theoretical calculations of dipole-dipole broadened lines (homogeneous broadening) in Sec. III and exhibit agreement with our experimental results. The concentration-dependent inhomogeneous broadening, which we believe to be caused by an increase in Kohn-Vosko³ charge oscillations with increasing erbium concentrations, is discussed in Sec. IV along with our conclusions.

II. EXPERIMENTAL TECHNIQUES AND RESULTS

Small balls of Ag:Er were prepared in an arc furnace under an argon atmosphere. The RESR samples were then made by filing these balls with a tungsten carbide

file to make powders for the spectrometers. In order to determine if any of the erbium was being lost during the arc-melting process, the remainder of three balls for three different concentrations (250, 1500, 2000 atomic ppm) were cold rolled and annealed. We then compared the residual resistivity ratios with those found earlier for Ag:Er.⁴ The only significant discrepancy was that of the nominal 250-ppm sample, which exhibited a resistivity appropriate to a concentration of 150 ppm.

The linewidth measurements were made at 9.2 and 1.7 GHz. The 9.2-GHz spectrometer consisted of a Varian E-101 microwave bridge and a cylindrical TE₀₁₁ cavity, and data were taken from 4.2 to 1.45 K. The 1.7-GHz spectrometer was a simple homodyne type that utilized a one-quarter wavelength stripline cavity with an unloaded Q of ≈ 400 . Data were taken with this spectrometer from 4.2 to 1.3 K. Further details on this spectrometer will be presented elsewhere.

The residual linewidth for each concentration at both frequencies was found by plotting the linewidths versus temperature and extrapolating to $T = 0$ K. The slope of the lines was taken to be the Korringa rate, proportional to $\langle J^2 \rangle$, and the 0-K intercept was defined as the residual linewidth. As expected, the Korringa rate is the same at both frequencies, independent of concentration (unbottlenecked regime). The square of the exchange, extracted from the temperature-dependent width, agrees within the error bars with the value of $\langle J^2 \rangle$ reported previously.⁵

Next, the residual linewidth was plotted as a function of concentration for both frequencies. These plots were found to be linear in concentration, and a least-squares fit to a straight line was made. These results are shown in Fig. 1. The slopes of the two lines (27.4 G/1000 ppm at 9 GHz and 11.5 G/1000 ppm at 1.7 GHz) do not scale linearly with frequency, nor are they equal. It is assumed, therefore, that there is both homogeneous and inhomogeneous

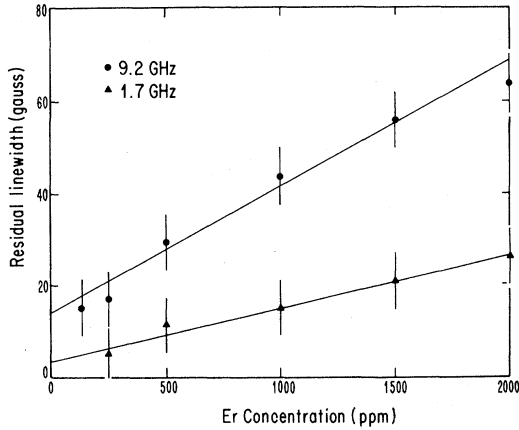


FIG. 1. Residual ($T=0$) linewidth of Er:Ag vs Er concentration at 9.2 and 1.7 GHz.

broadening associated with the erbium impurities. We also noted that the extrapolated 0-ppm linewidths are not equal, but scale with frequency, implying some form of concentration-independent inhomogeneous broadening.

In order to separate the homogeneous and inhomogeneous contributions to the concentration-dependent linewidth, the slopes of the two linewidth-versus-concentration plots were in turn plotted as a function of frequency. This enabled us to determine the inhomogeneous concentration dependence (the slope of the line) and the homogeneous concentration dependence (zero-frequency intercept) of the residual linewidths. The residual linewidth was then taken to be of the form $ac + bcf$, where c is the concentration in 1000 ppm, and f is the frequency in GHz. Our

data yielded $a = 8.0 \pm 5.0$ G/1000 ppm, and $b = 2.1 \pm 0.8$ G/1000 ppm f (GHz).

III. COMPARISON OF THEORY WITH EXPERIMENTAL RESULTS

In consideration of the above experimental results, we fit a $T=0$ linewidth to the form $ac + bcf + df$. The first two terms are the concentration-dependent homogeneous and inhomogeneous broadening, respectively, and the last is the concentration-independent inhomogeneous broadening.

We shall show the first term to be explained by dipole-dipole interactions. The second term is believed to be due to an increase in charge oscillations introduced into the lattice with increasing Er concentration. The third term is thought to be caused by residual strain in the lattice arising from the unannealed filed sample hosts.

We shall concentrate on the dipole linewidth, utilizing the classic paper by Van Vleck.⁶ He calculates the second and fourth moments of an RESR spectra in which every lattice site is occupied by a paramagnetic ion. The Hamiltonian consists of the usual Zeeman term, an isotropic exchange term, and a dipole-dipole energy term. The second moment is given by

$$\langle \Delta\nu^2 \rangle_{av} = -\text{Tr}[HS_x - S_x H]^2 / h^2 \text{Tr}(S_x)^2,$$

while the fourth moment equals

$$\langle \Delta\nu^4 \rangle_{av} = \text{Tr}[HU - UH]^2 / h^4 \text{Tr}(S_x)^2.$$

Here, Tr stands for trace, H is the above-mentioned Hamiltonian, S_x is the x component of the spin, $U = HS_x$, and h is Planck's constant. Using commutation and trace relationships, Van Vleck finds⁶

$$\langle \Delta\nu^2 \rangle_{av} = \frac{N^{-1}}{3} S(S+1) h^{-2} \sum_{jk} B_{jk}^2 \quad (1)$$

and

$$\begin{aligned} \langle \Delta\nu^4 \rangle_{av} = & h^{-4} N^{-1} \sum_{jkl \neq} [3B_{jk}^2 B_{jl}^2 + 2A_{jk}^2 (B_{jl} - B_{kl})^2 + 2A_{jk} A_{kl} (B_{jl} - B_{jk})(B_{jl} - B_{kl}) + 2A_{jk} B_{jk} (B_{jl} - B_{kl})^2] \\ & \times [\frac{1}{3} S(S+1)]^2 + 2N^{-1} \sum_{k>j} \{ B_{jk}^4 \frac{1}{5} [S^2(S+1)^2 - \frac{1}{3} S(S+1)] + 2B_{jk}^3 A_{jk} \frac{1}{5} [\frac{2}{3} S^2(S+1)^2 - \frac{1}{2} S(S+1)] \\ & + \frac{1}{2} B_{jk}^2 A_{jk}^2 [\frac{4}{5} S^2(S+1)^2 - \frac{3}{5} S(S+1)] \}, \quad (2) \end{aligned}$$

where N is the number of atoms in the crystal, S is the effective spin, and the sums over all lattice sites with $j, k, l \neq$ signifying no indices are allowed equal. Further,

$$B_{jk} = -3g^2 \mu_B^2 r_{jk}^{-3} (\frac{3}{2} \gamma_{jk}^2 - \frac{1}{2}),$$

$$A_{jk} = \tilde{A}_{jk} + g^2 \mu_B^2 r_{jk}^{-3} (\frac{3}{2} \gamma_{jk}^2 - \frac{1}{2}),$$

where g is the effective g value [for Er,

$g(\Gamma_7) = 6.8$], μ_B is the Bohr magneton, r_{jk} the distance from the ion in question to the other site, γ_{jk} the direction cosine between \vec{r}_{jk} and the applied external field, and \tilde{A}_{jk} is the exchange energy between two sites [either direct or indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange⁷].

Kittel and Abrahams⁸ have modified these equations to the case of every site not being occupied by a paramagnetic ion. They show that, for concentrations

below 10 000 ppm, the line shape is Lorentzian and the linewidth is proportional to the concentration. The concentration dependence can be easily seen by looking at the sums of Eqs. (1) and (2). If we assume that site j is occupied, then the sum in Eq. (1) and the second sum in Eq. (2) are only affected by the probability of site k being occupied. This would make them proportional to the concentration (c). The first sum in Eq. (2) would be dependent upon both the k and l sites being occupied, making this term proportional to c^2 . We shall neglect such terms because our largest concentration is 2000 ppm, so that c^2 is very small. Examining the exchange-dependent part of the fourth moment, we see both of these terms are identically equal to zero for a spin- $\frac{1}{2}$ moment. The erbium moment has a Γ_7 ground state, and the Γ_8 is believed to be 35 K higher in energy.⁹ We may therefore safely assign the erbium moment a fictitious spin $\frac{1}{2}$, removing the exchange dependence from the linewidth.

This leaves us with a concentration-dependent second and fourth moment of the form

$$\langle \Delta\nu^2 \rangle_{av} = \frac{250c}{h^2} \sum_k B_{jk}^2,$$

$$\langle \Delta\nu^4 \rangle_{av} = \frac{62.5c}{h^4} \sum_k B_{jk}^4.$$

Following Abragam,¹⁰ we find the linewidth for a Lorentzian line shape to be

$$\Delta\nu_{1/2} = (\pi/2\sqrt{3}) \langle \Delta\nu^2 \rangle_{av}^{3/2} / \langle \Delta\nu^4 \rangle_{av}^{1/2}.$$

Behringer¹¹ has calculated the geometrical portion of $\Delta\nu_{1/2}$ for a face-centered-cubic lattice out to fifteen nearest neighbors for a randomly oriented powder. Utilizing his calculation, we find a linewidth of 12.5 G/1000 ppm, roughly in agreement with the experimentally observed linewidths (≈ 8 G/1000 ppm).

IV. CONCLUSIONS

The concentration-independent and frequency-dependent broadening observed in the Ag:Er RESR is believed to be associated with residual strain in the silver lattice. We therefore label this component of the residual width inhomogeneous. This "residual" strain is random in magnitude and direction throughout the lattice. The sensitivity of the Ag:Er g value to the magnitude of the strain, and the angle between the strain axis and B -field direction, results in a distribution of g values. Arbilly *et al.*¹² derive an equation for the g value as a function of the angle between the strain axis and the applied B field. If we assume the strain is uniform in the silver lattice, and that only the angle is random, we can calculate a rms Δg , proportional to the observed linewidth. Following this approach, we find $\Delta g_{11}/g$ to be (in the notation of Arbilly *et al.*) ≈ 0.04 . Dodds *et al.*¹³ have found a

value of $\Delta g_{11}/g = 0.02$ for Ag:Er on quartz, where the effective strain at the interface is $\approx 0.43\%$. Following this approach, we obtain an rms residual host strain of $\sim 1\%$. This may appear to be rather large at first, but we used unannealed filed powders as our samples, and one must consider that RESR investigates only spins within a skin depth of the sample's surface. The reason for not annealing the filed samples used in accumulating the ESR data was that the portion of the residual linewidth due to the strain could be easily removed, and the annealing process appeared to cause a loss of 100 ppm of erbium in the samples regardless of the initial concentration. The erbium loss was found to be in the annealing process and not the original arc melting by melting the same sample several times in the arc furnace and comparing the residual linewidth after each melting.

We believe the concentration- and frequency-dependent broadening to be due to Kohn-Vosko oscillations of the charge density caused by the difference in charge between the Er and Ag ions (2+). The charge oscillations would alter the static crystalline field seen by the Er ions and, in effect, mix the Γ_7 and Γ_8 states. These comments lead us to believe that the frequency-independent broadening (which we label as homogeneous) is caused by dipole-dipole interactions, while the concentration- and frequency-dependent broadening (which we label as inhomogeneous) is attributed to Kohn-Vosko charge-density oscillations.

Other experiments could be done to verify these conclusions, but they are not without problems. One could repeat the experiment on single crystals and measure the angular variation of linewidth. However, sensitivity could be a problem when compared to the same concentration of Ag:Er in a powder, and careful orientation is important. A third frequency would appear to be useful since the use of only two frequencies in the above analysis is certainly a limitation. In this case if a frequency much lower than 1.7 GHz is chosen, a problem arises from the resonance field approaching 0 G. If a frequency much greater than 9.2 GHz is used, the random orientation of the erbium spins is no longer true, since the applied magnetic field for resonance would be large enough to cause some alignment of the erbium moments, and the dipole-dipole interaction linewidth as presented by Kittel and Abrahams cannot be utilized. A frequency between the two used here would give much less information as one would prefer the three frequencies to be widely separated. Finally, an S-state ion should be somewhat less sensitive to the strain in the lattice. In such a case, the slopes of the residual linewidth-versus-concentration curves at differing frequencies should be equal (i.e., homogeneous broadening only). In such a case, however, there are usually bottleneck problems that would have to be considered.

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