EPR study of cold-worked dilute gold-erbium alloys

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The results of an electron paramagnetic resonance (EPR) study of the effects of cold-working (rolling and polishing) on the EPR spectrum of Er in Au are reported. Pellets of dilute alloys of Au doped with Er were prepared in an arc furnace. From the pellets, samples were made by rolling at room temperature. The resonance experiments were carried out at X-band and at temperatures between 1.65 and 4.2 K. Heating of the rolled samples reduced the EPR linewidth and intensity and increased the asymmetry parameter (the A/B ratio). Gradual deformation by successive rolling resulted in almost complete recovery of the linewidth and A/B ratio to values observed before heating. No appreciable variations were detected in the g-factor, hyperfine structure constant or the Korringa relaxation rate.

Results are interpreted in terms of segregation of Er ions to subgrain boundaries. The EPR of magnetic impurities in metals appears to be a promising technique for the study of interactions between the magnetic impurities and the defects produced by cold-working.

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INTRODUCTION

The electron paramagnetic resonance (EPR) technique has been found to be a powerful tool for the investigation of the electronic properties of magnetic impurities in metals, of interactions between conduction electrons and magnetic impurities, and of interactions between the magnetic impurities themselves. The effects of cold-work on the conduction electron spin resonance (CESR) linewidth in pure metals was investigated by Beaune and Monod. The research reported here is the first demonstration of the application of the EPR of magnetic impurities to the study of effects produced in metals by cold-working.

EXPERIMENTAL

The alloys used in this study were prepared by melting 99.999% pure Au (supplied by Leco Industries Inc., N.Y., USA) with Er added as an impurity. An arc furnace with a water-cooled copper hearth was used for the melting. The samples in the form of small pellets were rolled at room temperature into plates and foils, by passing them through a manually operated roller at an average speed of approximately 2cm/sec. To prevent contamination of the samples with iron, the rolling was performed between 0.1mm thick tantalum sheets. A Varian Type EC-365 X-band EPR spectrometer with a standard liquid helium dewar and an immersed rectangular TE012 cavity was used.

RESULTS

Dilute gold-erbium alloys were studied using the EPR spectrum of the magnetic impurity Er. We shall refer to samples cold-worked by rolling at room temperature, which did not receive any other treatment prior to the EPR measurement, as "rolled" samples, and to samples heated (after rolling) for 1 hour at 400°C in a dynamic vacuum of 10^-6 torr, as "heated" samples. Typical EPR spectra recorded at 1.65K, of a "rolled" and a "heated" sample of Au doped with 100ppm Er are shown in Figs. 1a and 1b, respectively. The EPR linewidths $\Delta H$ were determined according to a procedure outlined in Ref. 3. The EPR linewidth of Er in Au, as a function of temperature T, can be expressed in our range of T, as $\Delta H = a + bT$, where $a$ represents the residual linewidth and $b$ the thermal broadening of the linewidth (the Korringa relaxation rate). EPR spectra were recorded at several temperatures between 1.65 and 4.2K. The values of $a$ and $b$ were determined by a least square best fit to the experimental $\Delta H$ values. The residual linewidths, asymmetry parameters A/B (the ratio between the maximum and minimum of the first derivative of the absorption line, for a definition see Fig. 1a), g-factors, hyperfine structure constants and Korringa relaxation rates in our rolled samples were the same as those reported for gold-erbium alloys prepared by filing. In heated samples drastic changes were observed in some of the above parameters: a decrease in the residual linewidth, an increase in the A/B
ratio and a decrease in the integrated intensity $I$ of the EPR line (i.e., a decrease in the number of Er ions contributing to the resonance line). The integrated intensity was obtained from the approximate expression $I = (A+B)(\Delta H)^2$. On the other hand, no changes were observed after heating in the g-factor, hyperfine structure constant and the Korringa relaxation rate.

![Diagram](Image)

**Fig. 1.** The EPR spectrum of Er in Au. Doping level = 1000ppm, $f = 9.46 GHz, T = 1.65K$.

- (a) - Rolled sample. A and B, the maximum and minimum of the first derivative of the absorption line, define the asymmetry parameter called the A/B ratio.
- (b) - Same sample after heating for 1 hour at 400°C in a vacuum of 10⁻⁶ torr.

The effects of gradual deformation on the features of the EPR line of Er were studied in an Au sample with a nominal concentration of Er of 1000ppm and a thickness of 0.75mm, prepared by rolling. The residual linewidth and A/B ratio in this rolled sample were 26.6G and 2.6, respectively. Heating of the sample (for 1 hour at 400°C in vacuum) reduced the residual linewidth to 12.5G and increased the A/B ratio to 4.7. Thereafter the sample was successively rolled down to thicknesses of 0.53, 0.25 and 0.15mm.

The EPR spectrum was recorded after each rolling. The residual linewidths and the A/B ratios are plotted as a function of cold-work $\Delta h/h_o$ in Fig. 2. A successful recovery of the linewidth and A/B ratio are clearly demonstrated in this figure. Thus for $\Delta h/h_o = 0.8$ most of the linewidth and A/B ratio are recovered. The integrated intensity of the resonance line and the concentration C of Er ions contributing to the resonance line increased as a function of cold-work. The behavior of I and C is summarized in Table I.

**TABLE I.** Increase in I, the integrated intensity of the resonance line, and C, the Er concentration contributing to the resonance line as a function of cold-working in a sample of Au doped with 1000ppm Er. The integrated intensity of the 0.75mm thick rolled sample was taken as 1.

<table>
<thead>
<tr>
<th>d (mm)</th>
<th>0.75</th>
<th>0.75</th>
<th>0.33</th>
<th>0.25</th>
<th>0.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta h/h_o$</td>
<td>0</td>
<td>-</td>
<td>0.29</td>
<td>0.67</td>
<td>0.8</td>
</tr>
<tr>
<td>$b$</td>
<td>1</td>
<td>0.05</td>
<td>0.05</td>
<td>0.17</td>
<td>0.37</td>
</tr>
<tr>
<td>C (ppm)</td>
<td>1000</td>
<td>130</td>
<td>130</td>
<td>310</td>
<td>515</td>
</tr>
</tbody>
</table>

The factor d is the sample thickness.

b. I was calculated from the approximate expression $I = (A+B)(\Delta H)^2$. Corrections were made for spectrometer gain and sensitivity.

c. In the estimation of C changes in the skin depth were taken into account.

Another way to recover $\Delta h/h_o$, I and C is by mechanical polishing. A few microns were removed from a 0.1mm thick heated sample by polishing the side pasted to the EPR cavity during the measurements. Care was taken to protect the other side of the sample, which is measured by EPR, against direct mechanical damage. This treatment resulted in full recovery of the residual linewidth, A/B ratio, intensity and Er concentration contributing to the resonance line.

**DISCUSSION**

In the previous section we described the changes produced by heating in the parameters of the EPR line of Er in Au, as well as the recovery of the values of the parameters by cold-working (rolling and polishing).

To explain the decrease in the linewidth and in the integrated intensity after heating we propose the following model, based on the segregation of Er ions to dislocations. During heating a thermally activated motion of dislocations (and subgrain boundaries) occurs. During this process dislocations come locked at Er ions, thus effectively Er ions are trapped at dislocations. These trapped Er ions do not contribute to the resonance line, since they are exposed to a crystalline field of lower symmetry than cubic. The process of segregation of impurities to dislocations causes a decrease in the linewidth due to two effects acting in parallel, one is a decrease in the number of Er ions contributing to the resonance line, which decreases the spin-spin and the Kohn-Vosko interactions, the other is the decrease in the stress field after heating. The first also causes a decrease in the integrated intensity. Linear recovery of the linewidth as a function of cold-work, as shown in Fig. 2, strongly suggests direct dependence of the linewidth on the production and movement of dislocations during rolling. The recovery of $\Delta h$, I and A/B after the polishing of heated samples also confirms our model of dislocation.
movement. It is well-known that mechanical polishing and deformation by rolling introduces dislocations in metals and causes them to move through the metal. Thus dislocations can move away from the Er ions, and the latter "freed from dislocations", can again contribute to the resonance line.

We have examined the possibility as to whether the changes in the features of the EPR line, caused by heating, might be due to oxidation, or clustering, or diffusion to the surface (causing a change in the concentration of Er in a surface layer), or changes in the valence state of Er$^{3+}$. Experiments where heating took place in air, hydrogen, or argon showed approximately the same effect on the EPR line as heating in vacuum. This excludes the possibility of appreciable oxygen diffusion into the samples. This result is consistent with the work of Svoboda$^9$ who studied the internal oxidation of impurities in gold. He showed extremely low solubility of oxygen in gold upon heating in air or in a low pressure oxygen atmosphere. It should be pointed out here that the solubility of Er in Au is good. It was reported$^{10}$ that at 400°C the solubility of Er in Au is about 0.5 at.%.

The polishing experiments also confirm that heating of our samples for 1 hour at 400°C does not cause oxidation, clustering, diffusion or valency changes of Er$^{3+}$ in gold.

By EPR one examines only a thin surface layer of the metal. The dominant contribution to the resistivity is due to the Er ions dissolved in the lattice. The skin depth in Au with 1000 ppm Er is about 4500Å.

Several models were considered to explain the significant increase of the A/B ratio after heating. At this stage we have no rigorous explanation for the behavior of the A/B ratio and more theoretical and experimental work is in progress.

SUMMARY

We have shown that the EPR of magnetic impurities in metals can be used to study effects produced in metals by cold-working. A detailed investigation of the changes in the features of the resonance lines of Er$^{3+}$ in Au, in samples cold-worked (rolled and polished) and heat treated, provided information on the segregation of Er$^{3+}$ ions to dislocations (subgrain boundaries), on the local strain around the magnetic impurities and on the influence of the different treatments on the number of Er ions contributing to the resonance line.

REFERENCES

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