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EPR of Fe in Superparamagnetic Alloys

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(21. V. 70)

Abstract. EPR measurements were carried out for $\text{Fe}_x\text{V}_{1-x}$ and $\text{Fe}_{.50}\text{Ti}_{.50}$ alloys. Their paramagnetic behavior is compared with NMR, magnetic susceptibility and specific heat data and explained in terms of superparamagnetism.

Introduction

The goal of the present investigation had been to extend the electron paramagnetic resonance studies of Gd as an impurity in high susceptibility metallic alloys as described in the work of Peter et al. [1]. However, a strong resonance absorption was observed in the host alloy even when the Gd impurity was not present. The $\text{Fe}_x\text{V}_{1-x}$ and $\text{Fe}_{.50}\text{Ti}_{.50}$ alloys investigated had one particular characteristic which appears to be shared by NiRh [2, 3] and several other alloys of Fe and Ni [4]: they exhibit superparamagnetic behavior. We interpret the resonance absorption as being due to iron-rich superparamagnetic clusters.

Preparation of Samples

The samples were prepared by arc melting requisite amounts of constituents under an argon atmosphere. The stated purity of the Fe used was 5 N and that of the V and Ti was 3 N. The EPR-measurements were made on powders produced with a tungsten carbide file from unannealed ingots. Unannealed ingots were used because annealing had a tendency to first decrease and then increase dramatically the density and volume of the iron-rich clusters. For example, one unannealed $\text{Fe}_{.20}\text{V}_{.80}$ sample showed no superparamagnetic behavior down to nitrogen temperature, while after annealing a large resonance was observed at room temperature. This tendency for the clusters to grow upon annealing reflects the instability of the lattice near the phase boundary, which is the reason that inhomogeneous iron distribution is observed in these alloys.

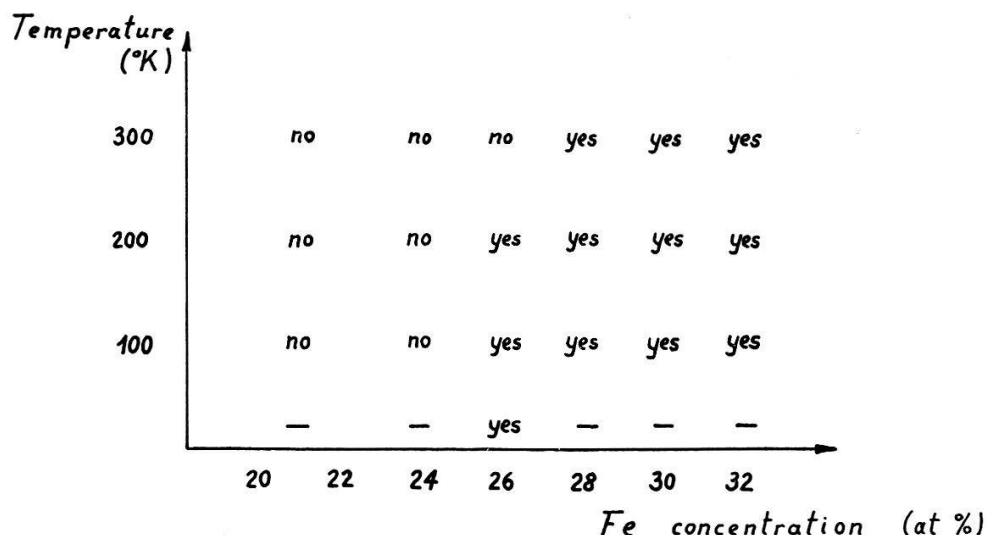
EPR Measurements

The EPR measurements were carried out at a frequency of 35 Gc for both samples and at 70 Gc for $\text{Fe}_{.50}\text{Ti}_{.50}$. The occurrence of the resonance coincides quite

well with other measurements on these alloys such as the dependence of magnetic susceptibility and NMR linewidths [4] on temperature and concentration, and the appearance of a low temperature anomaly in the specific heat [5, 6].

This occurrence is shown in Table I as a function of concentration and temperature.

Table I
Occurrence of resonance as a function of concentration and temperature for $V_{1-x}Fe_x$ alloys.



For the $V_{1-x}Fe_x$ alloys, the g value is shown in Figure 1 and the linewidth in Figure 2 as a function of temperature for an iron concentration of 26 atomic percent. For this alloy the EPR signal decreased gradually in amplitude as the temperature was increased, becoming too small to distinguish above 250°K. No systematic variation of g value or linewidth with concentration was found.

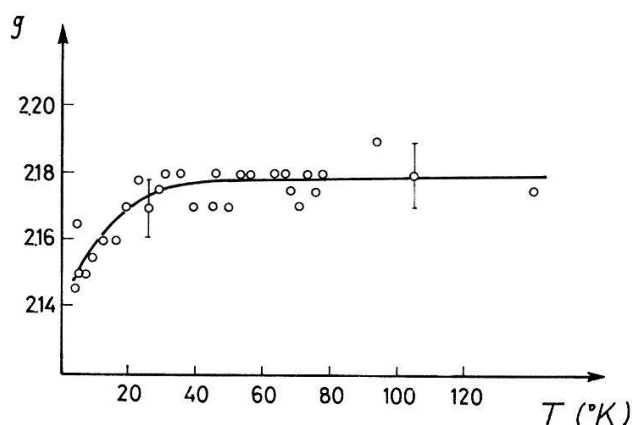


Figure 1
 g -value as a function of temperature for the $V_{.74}Fe_{.26}$ alloy.

For $Fe_{.50}Ti_{.50}$ alloy, a value $g = 2.16 (\pm 0.01)$ with a linewidth $470 (\pm 50)$ Oe was found at room temperature at 35 Gc. At 70 Gc, the same g -value was observed but the linewidth broadened to 1,110 Oe. At nitrogen temperature, the 35 Gc g -value increased to 2.19 and the linewidth to $810 (\pm 50)$ Oe.

The observation of paramagnetic resonance of Fe has only been reported in one other metallic alloy $Cr_{1-x}Fe_x$ for Fe concentrations x of 1.9 and 3.6 atomic percent [7].

In the paramagnetic region the g -value is temperature independent while the linewidth decreases slightly as the temperature is increased. This behavior is analogous to that found for $V_{1-x}Fe_x$ and to a lesser extent to that for $Fe_{.50}Ti_{.50}$. From the large increase in linewidth at 70 Gc for $Fe_{.50}Ti_{.50}$ it is apparent that inhomogeneous broadening is important here. The observation that there is no Korringa-type linewidth broadening at higher temperatures might suggest that iron-electron coupling J_{sd} is small. However, it is more likely that the line is exchange narrowed, so that variations in this narrowing with temperature offset any Korringa-type broadening.

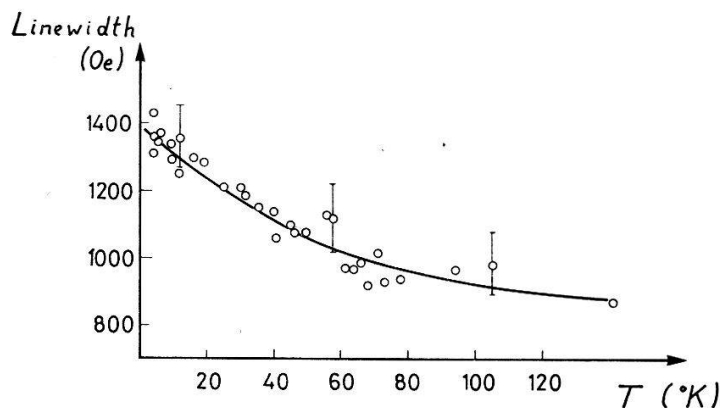


Figure 2
EPR linewidth as a function of temperature for the $V_{.74}Fe_{.26}$ alloy.

Discussion and Comparison with Known Experimental Results

A. Magnetic Susceptibility

Magnetic measurements of $V_{1-x}Fe_x$ [4, 8] and $Fe_{.50}Ti_{.50}$ [6] show that to temperatures below liquid nitrogen temperature the alloys are not ferromagnetic and that the susceptibility can be explained as superparamagnetic behavior. The magnetic susceptibility of $V_{1-x}Fe_x$ found by Bretthauer [8] is shown as a function of iron concentration x in Figure 3. As x approaches the value 31 atomic percent, the increase in magnitude of the susceptibility indicates that the superparamagnetic cluster density increases as the cubic α -phase $V_{1-x}Fe_x$ lattice becomes less stable. The phase diagram given by Hansen [9] shows that the α -phase region extends just to this concentration x . The magnetic susceptibility is shown in Figure 4 as a function of temperature for an alloy with 22.4 atomic percent iron. It can be seen that the

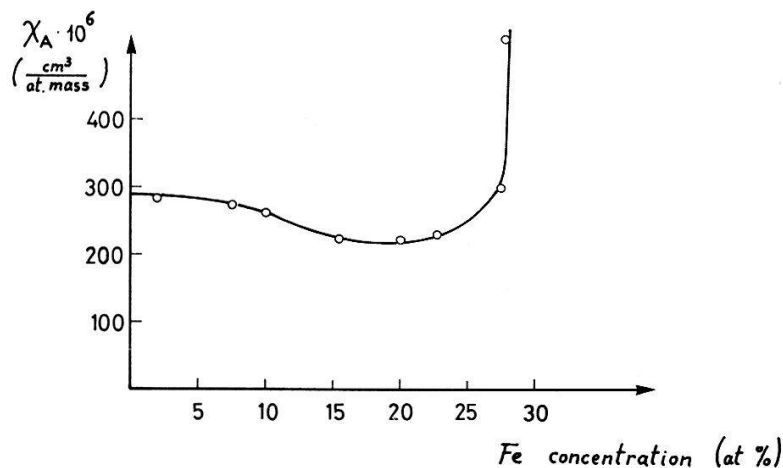


Figure 3
Magnetic susceptibility of $V_{1-x}Fe_x$ alloys for a temperature of 290°K (after Bretthauer [8]).

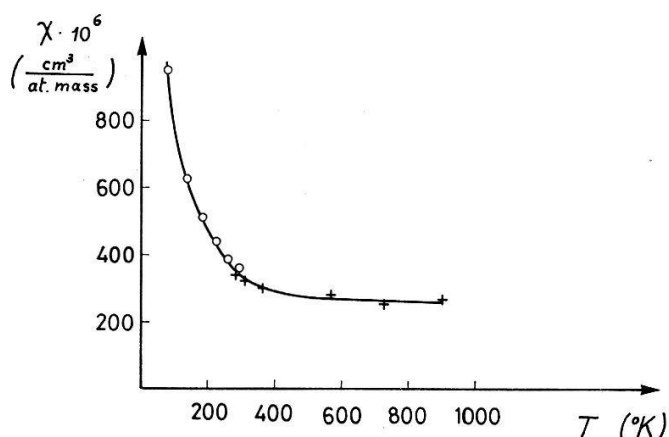


Figure 4
Magnetic susceptibility of $V_{1-x}Fe_x$ alloys for a concentration of 22.4 atomic percent Fe (after Bretthauer [8]).

susceptibility becomes strongly temperature dependent below about 400 °K, indicating that the Curie temperature of the superparamagnetic clusters must be of this order of magnitude for this particular alloy.

A common test establishing the existence of superparamagnetic behavior is the requirement that magnetization values M measured as a function of field H at different temperatures T should superpose on a single curve when M is plotted versus H/T . In a simple theory [10], the calculation of the magnetization of the moments, partially aligned by the field H and partially disordered by thermal motion, results in a Langevin function if the spontaneous magnetization per unit volume of the superparamagnetic clusters is found to be nearly independent of temperature.

Of course even in classical examples of superparamagnetic behavior a simple Langevin function is not observed because of the influence of cluster and composition which produces a distribution of Curie temperatures for the clusters.

The magnetization values measured for $Fe_{.50}Ti_{.50}$ can be superposed reasonably well on a plot of M versus H/T [6].

For $V_{1-x}Fe_x$ the magnetization follow a Langevin-type curve but do not superpose when plotted versus H/T [8]. The reason for this is that after Bretthauer the susceptibility takes the form:

$$\chi = \frac{C}{T + \theta(x)} + \chi_0(x)$$

where

$\theta(x)$ = concentration dependent Curie temperature,

$\chi_0(x)$ = concentration dependent, temperature independent contribution to the susceptibility.

In this case, the magnetization as a function of H/T yields not a single curve because (I) there are important contributions to the susceptibility which do not arise from the superparamagnetic clusters and (II) the different volumes and compositions of the clusters produce a distribution of Curie temperatures. Also, at sufficiently low temperatures some of the clusters may become stable, that is in certain orientations by crystalline anisotropy.

From the magnetic measurements on the alloys it appears that the following conclusions can be drawn:

1. For $V_{1-x}Fe_x$ at least above some characteristic temperature the clusters break up and we obtain just a temperature independent band susceptibility from the iron-rich regions of the alloy.
2. Above nitrogen temperature at least the alloys are behaving superparamagnetically, so what we observe with EPR is not a ferromagnetic resonance in the usual sense.
3. Superparamagnetic clusters are responsible for the magnetic behavior rather than localized moments associated with individual iron atoms. In fact, there is no reason to expect localized magnetic moment formation only for iron concentrations in excess of 20 atomic percent. In addition there is no reason to expect a localized moment to disappear as the temperature is increased (as shown in Fig. 4).

B. NMR

The NMR of V^{51} in $V_{1-x}Fe_x$ alloys has been done by Lam et al. [4]. At room temperature the linewidth increases fastly with iron concentration above 23 atomic percent. A rapid decrease of Knight shift also occurs above this concentration.

When the temperature is lowered for concentrations $x < 23$ atomic percent, the linewidth remains temperature independent, while for concentrations $x > 23$ atomic percent a broadening arises when the moments are established in the iron-rich clusters. As the iron concentration increases or as the temperature is lowered, the density of superparamagnetic clusters increases, hence the NMR line broadening.

C. Specific Heat

The specific heat of the $V_{1-x}Fe_x$ [5] and $Fe_{.50}Ti_{.50}$ [6] alloys, along with some other alloys containing Fe and Ni exhibits an anomalous specific heat at low temperatures. This is represented by the term $A(T)$ in the equation

$$C = A(T) + \gamma T + \beta T^3$$

and it appears as an upturn at low temperatures, $A(T)/T$, when the specific heat is plotted as C/T versus T^2 .

The theory of electron-paramagnon interactions had been used to discuss this anomaly; but Hahn and Wohlfarth [3] questioned this interpretation and pointed out that it could as well be explained in terms of superparamagnetic effects. It is not possible to establish with certainty that their explanation is the proper one for these alloys, but two assertions can be made:

1. Above 4.2°K the $V_{1-x}Fe_x$ alloy has been observed to exhibit superparamagnetic behavior.
2. The variation of the low temperature anomaly $A(T)$ with concentration does not accord well with the explanation involving paramagnon interactions.

The anomalous upturn associated with $A(T)$ appears only for Fe concentrations

above 20 atomic percent and disappears at concentrations higher than 31 atomic percent, where it is known that $V_{1-x}Fe_x$ is ferromagnetic at these temperatures [4, 8, 11].

Conclusion

In summary we have observed a paramagnetic resonance of $V_{1-x}Fe_x$ alloys and of $Fe_{.50}Ti_{.50}$. By comparing temperature and concentration dependence of these measurements with magnetic susceptibility, NMR and specific heat results which have been published we have shown that the origin of the resonance lies in iron-rich clusters in the alloy which behave superparamagnetically.

Because the lattice is unstable in these alloys near a phase transition, the alloys are strongly affected by different heat treatments and the characteristics are not reproducibly uniform. Measurements made by different workers on different samples are thus difficult to compare. It is suggested that a study of some of these superparamagnetic alloys by means of EPR, NMR, magnetic susceptibility and specific heat made on identically the same specimens could yield precise comparative data. These precise data, including EPR g -values and linewidth values might be of assistance to theoreticians in developing a more detailed description of some characteristics of these superparamagnetic clusters which are not well established at present; for example the nature of the anisotropy energy in the alloys or the polarization of the matrix produced by the large moments of the clusters.

Acknowledgments

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REFERENCES

- [1] M. PETER, J. DUPRAZ and H. COTTET, *Helv. phys. Acta* **40**, 301 (1967).
- [2] H. COTTET, P. DONZÉ, J. ORTELLI, E. WALKER et M. PETER, *Helv. phys. Acta* **41**, 755 (1968).
- [3] A. HAHN and E. P. WOHLFARTH, *Helv. phys. Acta* **41**, 857 (1968).
- [4] D. J. LAM, D. O. VAN OSTENBURG, M. V. NEVITT, H. D. TRAPP and D. W. PRACHT, *Phys. Rev.* **131**, 1428 (1963).
- [5] C. H. CHENG, C. T. WEI and P. A. BECK, *Phys. Rev.* **120**, 426 (1960).
- [6] K. SCHRÖDER and C. H. CHENG, *J. appl. Phys.* **31**, 2154 (1960).
- [7] M. B. SALAMON and F. J. FEIGL, *J. Phys. Chem. Solids* **29**, 1443 (1968).
- [8] K. BRETTAUER, Diplomarbeit, Marburg 1965 (unpublished).
- [9] M. HANSEN, *Constitution of Binary Alloys*, 1958.
- [10] C. P. BEAN and J. D. LIVINGSTON, *J. appl. Phys.* **30** Suppl., 120 S (1959).
- [11] M. V. NEVITT and A. T. ALDRED, *J. appl. Phys.* **34**, 463 (1963).