Effect of magnetic iron impurity on the superconducting properties of an amorphous $Nb_{50}Zr_{35}Si_{15}$ alloy

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The effect of magnetic iron impurity on the superconducting properties of amorphous $Nb_{50}Zr_{35-x}Si_{15}Fe_x$ ($x \leqslant 4$ at %) alloys was examined. Doping with an iron impurity resulted in a linear depression of T_c and $H_{c2}(T)$ and a decrease in $-(dH_{c2}/dT)_{T_c}$ and ρ_n after reaching a maximum value at 0.5 to 1.0 at % iron. The observed decrease was about 35% for T_c, 85% for H_{c2} at 2.0 K, 16% for $-(dH_{c2}/dT)_{T_c}$ and 21% for ρ_n. Although the decrease in $-(dH_{c2}/dT)_{T_c}$ occurs through the decrease in ρ_n as expected from the GLAG theory, the depression in T_c caused by magnetic impurity could not be explained in terms of the GLAG theory which is applicable to Nb–Zr–Si amorphous alloys without magnetic impurity, but was interpreted as arising from the pair-breaking effect in the superconducting nature due to magnetic scattering. However, the pair-breaking effect was found to be smaller by about one-tenth for the present amorphous superconductors than for crystalline superconductors, indicating the high stability of the superconductivity of the Nb–Zr–Si–Fe alloys against the magnetic scattering arising from the magnetic impurity. The reduced magnetic field at which the reduced fluxoid pinning force exhibits a maximum value increased with iron concentration, indicative of an enhancement of fluxoid pinning force. The enhancement in fluxoid pinning force was interpreted as arising from the increase in compositional, electronic and/or magnetic fluctuations by the dope of iron impurity.

1. Introduction

A large number of studies has been carried out on the effect of magnetic impurities on the superconductivity of crystalline metals and alloys and many interesting phenomena have been clarified. The superconductivity of crystalline metals and alloys is strongly affected by small amounts of magnetic impurities. The doping of crystalline superconductors with magnetic impurities results in an extremely significant depression of T_c and a decrease in the superconducting gap energy, owing to a pair-breaking effect caused by magnetic scattering, even though the amount of dopant is quite small. Further increase in magnetic impurity results in a complete disappearance of the superconducting state.

On the other hand, in an amorphous phase having a long-range random atomic configuration, the normal electrical resistivity, which is closely related to the superconducting properties, is little changed by doping with a small amount of magnetic elements. Furthermore, the change in electronic density of states at the Fermi level with alloy composition for amorphous superconductors is very smooth, probably because of the extremely short mean free path of electrons [1], in contrast to the abrupt change in crystalline superconductors. From these results the degra-

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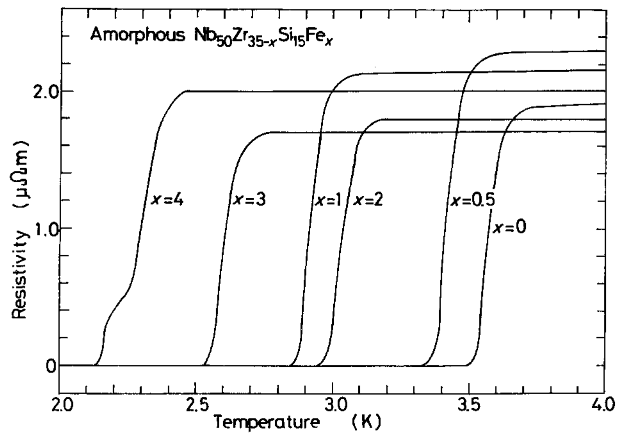

Figure 1 Change in the electrical resistivity near T_c with iron concentration for amorphous $Nb_{50}Zr_{35-x}Si_{15}Fe_x$ alloys.

dation of the superconductivity caused by impurities is expected to be much smaller for amorphous alloys than for crystalline alloys. Additionally, when an impurity element with a magnetic moment is doped into a homogeneously amorphous phase without any defects which act as effective pinning centres, the electronic and magnetic fluctuations in the amorphous phase seem to become large, resulting in increases in superconducting transition width (ΔT_c) and $J_c(H)$ and a depression of the appearance of flux flow resistivity $\rho_f(H)$.

In this paper, we present the effect of magnetic iron impurity on the superconducting properties of an amorphous $Nb_{50}Zr_{35}Si_{15}$ alloy. The main purposes of the present study were:

1. determination of the critical iron content for the complete destruction of superconductivity, and the rate of depression of T_c per 1 at% iron, and

2. to ascertain whether or not magnetic and electronic fluctuations in the amorphous phase arising from the iron impurity have an effect on the values of ΔT_c, $J_c(H)$ and $\rho_f(H)$.

2. Experimental methods

$Nb_{50}Zr_{35-x}Si_{15}Fe_x$ alloys of different iron concentration ($x = 0$, 1, 2, 3 and 4 at%) were prealloyed under a purified and gettered argon atmosphere in an arc furnace on a water-cooled copper mould from niobium (99.5 wt%) containing 0.085 wt% oxygen, 0.078 wt % tantalum and 0.008 wt% carbon, etc, impurities, zirconium (99.6 wt%) containing 0.086 wt% oxygen, 0.051 wt% iron and 0.014 wt% chromium, etc, impurities, silicon (99.999 wt%) and iron (99.99 wt%). The weight of the mixture melted in one run was about 30 g. The ingots were repeatedly turned over and remelted to ensure homogeneity. The compositions of the alloys reported are the nominal because the losses during melting were negligible.

The technique and apparatus for fabricating ribbon samples having a typical cross-section of about 20 μm × 1 mm and the method of characterizing the amorphous nature of the samples by X-ray and electron metallographic techniques, have been described elsewhere [2]. Measurements of superconducting properties T_c, $H_{c2}(T)$, $J_c(H)$ and $\rho_f(H)$ were done resistively using a conventional four-probe technique. The critical current was defined as the threshold current at which non-zero voltage (> 1 μV) was first detected. The temperature was measured to within ± 0.01 K using a calibrated germanium thermometer. A magnetic field up to 7.2×10^6 A m^{-1} was applied transversely to the specimen surface and feed current.

3. Results

Fig. 1 shows the change in electrical resistivity of an amorphous $Nb_{50}Zr_{35}Si_{15}$ alloy near T_c with the replacement of zirconium by iron. The features of this figure are summarized as follows:

1. T_c is depressed by the dope of iron and the rate of the depression is approximately proportional to the iron concentration (x);

2. The superconducting transition becomes slightly broader and the value of ΔT_c increases from 0.01 K at 0 at% iron to 0.22 K at 4 at% iron;

3. The normal electrical resistivity (ρ_n) exhibits a maximum value near 0.5 to 1.0 at% Fe and tends to decrease with further increasing iron concen-

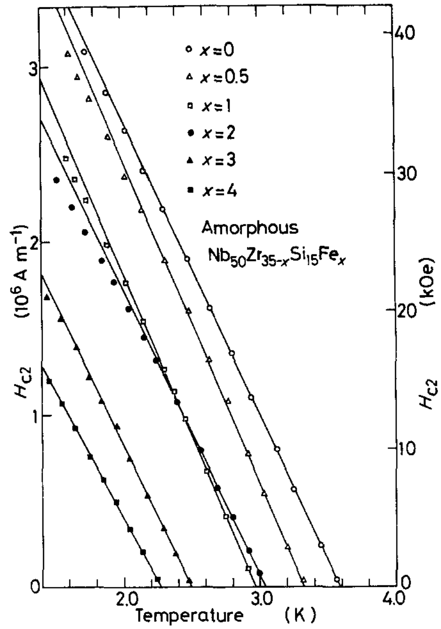

Figure 2 Change in the temperature dependence of upper critical field $H_{c2}(T)$ with iron concentration for amorphous $Nb_{50}Zr_{35-x}Si_{15}Fe_x$ alloys.

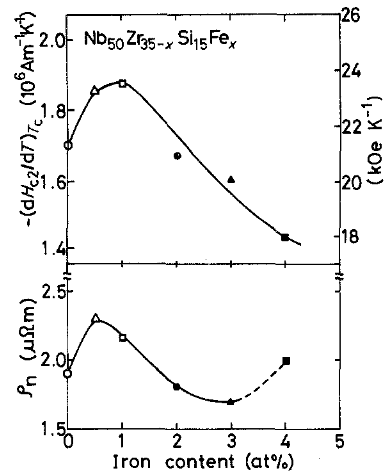

Figure 3 Changes in the temperature gradient of H_{c2} near T_c, $-(\mathrm{d}H_{c2}/\mathrm{d}T)_{T_c}$, and the normal electrical resistivity, ρ_n, at 4.2 K for amorphous $Nb_{50}Zr_{35-x}Si_{15}Fe_x$ alloys.

tration, if one is allowed to omit the data of the alloy containing 4 at% iron.

The upper critical magnetic field H_{c2} values near T_c as a function of temperature for $Nb_{50}Zr_{35-x}Si_{15}Fe_x$ amorphous alloys are shown in Fig. 2. $H_{c2}(T)$ decreases significantly with increasing iron content. Furthermore, the temperature gradient of H_{c2} near T_c, $-(\mathrm{d}H_{c2}/\mathrm{d}T)_{T_c}$, as a function of iron concentration for $Nb_{50}Zr_{35-x}Si_{15}Fe_x$ amorphous alloys is shown in Fig. 3, where the normal electrical resistivity ρ_n at 4.2 K is also given for reference. $-(\mathrm{d}H_{c2}/\mathrm{d}T)_{T_c}$ increases from 2.13 to 2.35 T K^{-1} when approaching 0.5 to 1.0 at% iron and then decreases to 1.80 T K^{-1} with further increase in iron concentration, similar to the composition dependence of ρ_n. Fig. 4 shows the correlation between $-(\mathrm{d}H_{c2}/\mathrm{d}T)_{T_c}$ and ρ_n for $Nb_{50}Zr_{35-x}Si_{15}Fe_x$ amorphous alloys. One can see a clear tendency that the higher is ρ_n the larger is $-(\mathrm{d}H_{c2}/\mathrm{d}T)_{T_c}$, suggesting that the change in the temperature gradient of H_{c2} near T_c with iron content occurs through the change in ρ_n as expected from the GLAG theory (e.g. [3]). However, changes in $-(\mathrm{d}H_{c2}/\mathrm{d}T)_{T_c}$ and ρ_n of $Nb_{50}Zr_{35-x}Si_{15}Fe_x$ alloys with iron concentration are different from that of T_c. This indicates that the composition dependence of T_c cannot be interpreted in terms of the GLAG theory [3] which has been recognized as being obeyed in Nb–Zr–Si amorphous alloys [4] without magnetic impurities.

Fig. 5 shows the change in $J_c(H)$ with iron concentration at about 1.5 K. The $J_c(H)$ degrades significantly with increasing iron concentration; for example, the value of J_c at $H = 1 \times 10^6$ A m^{-1} is 8.5×10^4 A m^{-2} at 0 at% iron and 0.37×10^4 A m^{-2} at 4 at% iron. A similar change in $J_c(H)$ with iron concentration was observed at different temperatures. The degradation of $J_c(H)$ is considered to originate from the depression of H_{c2}, but the effect of elemental iron on the fluxoid pinning force remains unanswered from this figure. A detailed investigation of this problem will be described later.

The change in $\rho_f(H)$ at about 1.5 K with iron

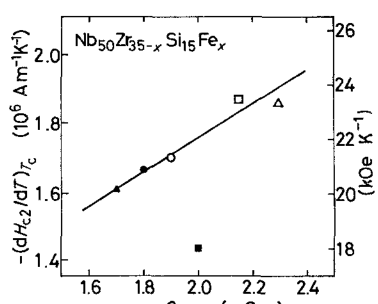

Figure 4 Correlation between the temperature gradient of H_{c2} near T_c, $-(\mathrm{d}H_{c2}/\mathrm{d}T)_{T_c}$ and the normal electrical resistivity, ρ_n, at 4.2 K for amorphous $Nb_{50}Zr_{35-x}Si_{15}Fe_x$ alloys.

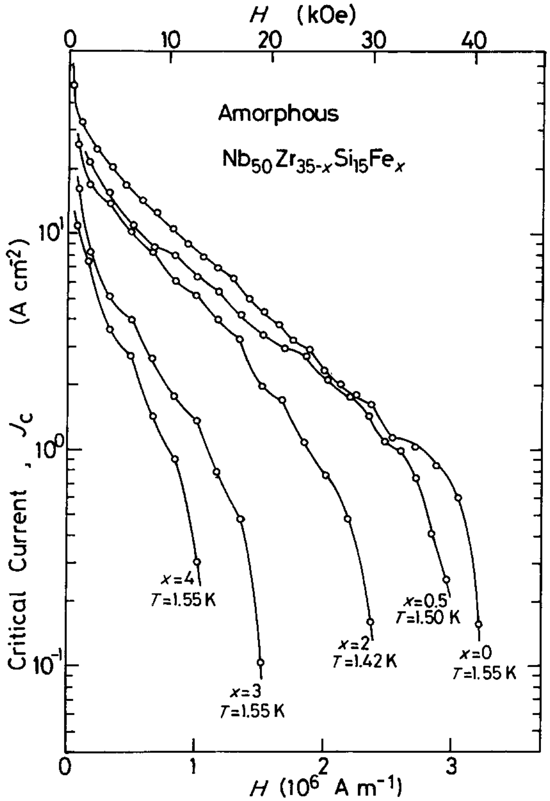

Figure 5 Change in the magnetic field dependence of the critical current density, $J_c(H)$, with iron concentration for amorphous $Nb_{50}Zr_{35-x}Si_{15}Fe_x$ alloys.

concentration is shown in Fig. 6. The linear part of the $\rho_f/\rho_n - H$ relation decreases significantly with increasing iron concentration, indicative of the depression of the flux flow resistivity. The arrows shown in the figure represent the value of H_{c2} which is defined as the field where ρ_f/ρ_n begins to deviate from unity. H_{c2} decreases from 3.7×10^6 to 1.7×10^6 A m^{-1} with increasing iron concentration. The hypothetical upper critical field at 0 K, determined only by the orbital effect $H_{c2}{}^*(0)$, was also estimated from the linear relationship between ρ_f/ρ_n and H using Kim's empirical law [5], $\rho_f/\rho_n = H/H_{c2}{}^*(0)$. If one assumes that the change in H_{c2} at 1.5 K with iron concentration is the same as that at 0 K, the discrepancy between $H_{c2}{}^*(0)$ and $H_{c2}(0)$ is said to increase remarkably with increasing iron concentration upon considering the well-known relationship (Equation 1) between $H_{c2}{}^*(0)$, $H_{c2}(0)$ and the upper critical field $H_p(0)$ by the full exertion of the Pauli–paramagnetic effect [6],

$$\frac{1}{H_{c2}(0)^2} = \frac{1}{H_{c2}{}^*(0)^2} + \frac{2}{H_p(0)^2}, \qquad (1)$$

the suppression of the upper critical field by iron impurity is concluded to originate from the Pauli–paramagnetic effect.

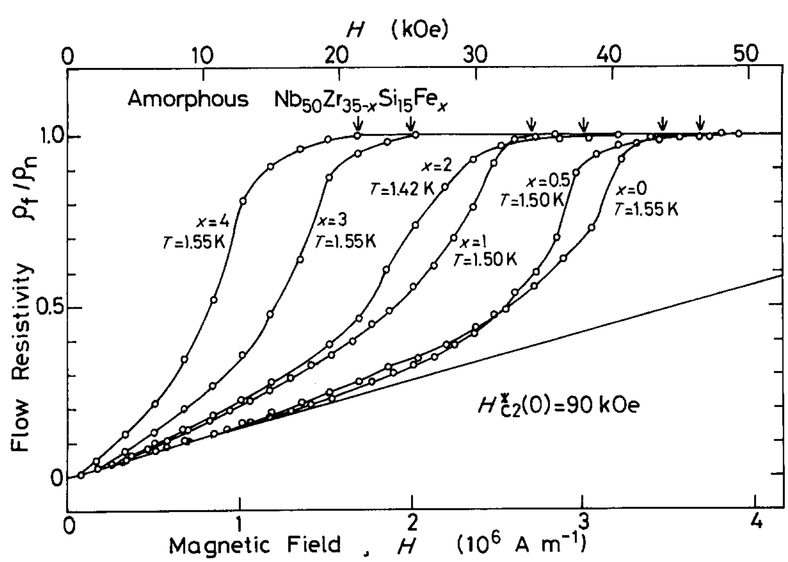

Figure 6 Change in the magnetic field dependence of flux flow resistivity ρ_f/ρ_n with iron concentration for amorphous $Nb_{50}Zr_{35-x}Si_{15}Fe_x$ alloys.

4. Discussion

4.1. The depression of T_c

Based on the data shown in Fig. 1, the ratio T_c/T_{co} as a function of iron concentration was plotted in Fig. 7, where T_{co} presents the transition temperature of the undoped alloy. As seen in the figure, T_c is depressed almost linearly with increasing iron concentration. The solid line in the figure represents a linear relationship between T_c/T_{co} and iron concentration obtained by the method of least squares and the correlation coefficient is 0.97, indicating the existence of a good linear relationship between T_c/T_{co} and x. From this relationship, the critical iron concentration, n_{cr}, at $T_c/T_{co} = 0$ is estimated to be 11.6 at%. Our previous paper [4] demonstrated the existence of a strong correlation between T_c and ρ_n for Nb–Zr–Si amorphous alloys without magnetic iron impurity, but T_c for Nb–Zr–Si–Fe alloys is significantly lowered by increasing iron content, different from the change in ρ_n with iron content. Thus, there is no strong correlation between T_c and ρ_n for the Nb–Zr–Si–Fe alloys containing magnetic iron impurity, suggesting that the depression of T_c by the dope of iron might originate from a pair-breaking effect in superconductors due to magnetic scattering [7].

Next we will try to interpret the depression of T_c for $Nb_{50}Zr_{35-x}Si_{15}Fe_x$ amorphous alloys in terms of the pair-breaking effect. The depression of T_c as a function of magnetic impurity concentration has been reported for a large number of crystalline superconductors and the trend of the change has been explained by the Abrikosov–Gor'kov (AG) theory [7]. For example, the superconductivity of a crystalline $LaAl_2$ alloy vanishes completely upon the addition of 1.7 at% cerium [8] and that of an amorphous

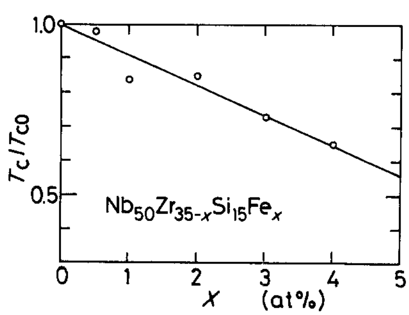

Figure 7 Change in the normalized superconducting transition temperature, T_c/T_{co}, with iron concentration for amorphous $Nb_{50}Zr_{35-x}Si_{15}Fe_x$ alloys.

$(Mo_{0.6}Ru_{0.4})_{80}P_{20}$ alloy by 1.6 at% iron [9]. On the other hand, the ratio of T_c/T_{co} for the present $Nb_{50}Zr_{35}Si_{15}$ alloy is as large as 0.65, even with a dope of 4 at% iron. Thus, the T_c values of the $Nb_{50}Zr_{35-x}Si_{15}Fe_x$ alloys are located at temperatures much higher than those predicted by the AG theory [7]. This indicates that the superconductivity of the present amorphous alloy is very stable against the magnetic impurity compared to crystalline superconductors and the molybdenum-based amorphous alloys.

The pair-breaking parameter (α/α_{cr}), which arises from scattering of conduction electrons by magnetic impurities, is estimated by the following expression [10]:

$$\left(\frac{\alpha}{\alpha_{cr}}\right)_{imp} = \frac{H_{c2}(c, T)}{H_{c2}(0, 0)} - \frac{H_{c2}(c, T)}{H_{c2}(0, 0)} - \frac{P}{P_{cr}}. \quad (2)$$

Here α_{cr} corresponds to $T_c = 0$ (complete destruction of superconductivity) and P/P_{cr} is the Pauli term due to polarization of the conduction band by the exchange field of the iron spins. From Equation 2, with $P/P_{cr} = 0$, the value of $(\alpha/\alpha_{cr})_{imp}$ for the Nb–Zr–Si–Fe amorphous alloy was found to vary in the range $\simeq 0.05$ to $\simeq 0.60$. Since the value of H_{c2} near $T = 0$ K has not yet been measured, $H_{c2}(0, 0)$ used in the calculation was approximated to be 5.52 T under the assumption that the temperature dependence of H_{c2} near $T = 0$ K is the same as that [11] of the actually measured amorphous $Zr_{85}Si_{15}$ alloy with the same metalloid composition. Furthermore, the values of $1/c$ (α/α_{cr}) were scattered between $\simeq 10$ and $\simeq 22$, being much larger than those (1 to 2) of crystalline superconductors such as (La, Ce)Al_2 [8], (La, Gd)Al_2 [12] and (La, Ce)$_3$In [13] etc, and that (0.8 to 1.1) of the $(Mo_{0.6}Ru_{0.4})_{80}P_{20}$ amorphous alloys [9]. This indicates that the degradation of superconductivity by the pair-breaking effect due to magnetic scattering of iron impurity is considerably smaller for the present Nb–Zr–Si amorphous alloy as compared with crystalline superconductors. However, the reason for such an extremely weak pair-breaking effect for the Nb–Zr–Si–Fe amorphous alloys remains unknown at present. A more detailed investigation of the superconductivity–breaking mechanism for amorphous superconductors of various alloy compositions will shed light on the problem of whether the high stability of the superconductivity against magnetic impurity for the present amorphous alloy is due to a common feature of an amorphous phase or due to the particular alloy composition of the Nb–Zr system.

4.2. Change in the fluxoid pinning force

It was shown in Fig. 5 that $J_c(H)$ degrades significntly with increasing iron concentration. Since the degradation of $J_c(H)$ is mainly attributed to the depression of H_{c2}, it is necessary to eliminate the influence of H_{c2} in order to obtain information on the change of the fluxoid pinning force by the dope of magnetic impurity. Based on the results shown in Fig. 5, the reduced pinning force, $P_v/P_{v,max}$, as a function of the reduced magnetic field b ($b = B/H_{c2}$), is shown in Fig. 8, where P_v was determined from $P_v = B \times J_c$. As seen in the figure, the position of $P_{v,max}$ shifts to the higher side of B/H_{c2} with increasing iron concentration, indicative of an enhancement of the fluxoid pinning force. This is probably because the dope of magnetic impurity into the amorphous phase causes an increase in the statistical fluctuation of magnetic impurity concentration in a volume on the range of coherence length. The increase in the inhomogeneity of the amorphous phase is also supported by the fact that the superconducting transition becomes broader with increasing iron concentration.

5. Conclusion

In order to examine the effect of magnetic impurity on the superconducting properties of an amorphous alloy, T_c, ΔT_c, $H_{c2}(T)$, $J_c(H)$ and $\rho_f(H)$

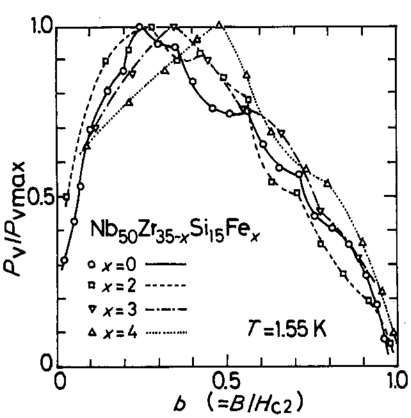

Figure 8 Change in the reduced magnetic field dependence of the normalized fluxoid pinning force, $P_v/P_{v,max}$, with iron concentration for amorphous $Nb_{50}Zr_{35-x}Si_{15}Fe_x$ alloys.

of amorphous $Nb_{50}Zr_{35-x}Si_{15}Fe_x$ alloys were measured as a function of iron concentration. The results obtained are summarized as follows.

1. The dope of iron impurity causes a slight increase in ΔT_c, a significant linear depression in T_c and $H_{c2}(T)$, and a decrease in $-(dH_{c2}/dT)_{T_c}$ and ρ_n after reaching a maximum value at 0.5 to 1.0 at % iron.

2. The linear depression in T_c is much smaller than that for crystalline superconductors and a $(Mo_{0.6}Ru_{0.4})_{80}P_{20}$ amorphous superconductor, indicating that the superconductivity of the present amorphous alloys is very stable against the magnetic scattering arising from the magnetic impurity.

3. The values of T_c of the Nb–Zr–Si–Fe alloys do not have a close relationship with ρ_n and $-(dH_{c2}/dT)_{T_c}$, which is a common feature for Nb–Zr–Si alloys without magnetic impurity, and hence depression of T_c by the dope of iron impurity was interpreted as arising from the pair-breaking effect in superconductivity due to magnetic scattering.

4. $J_c(H)$, as well as $\rho_f(H)$, decreases with increasing iron concentration owing to the depression in H_{c2}, when the characteristics are compared at the same temperature. However, the reduced magnetic field at which the reduced fluxoid pinning force exhibits a maximum value increases with increasing iron concentration in spite of the decrease in the reduced temperature ($t = T/T_c$), indicative of an enhancement of fluxoid pinning force. The enhancement in the pinning force was interpreted as originating from the increase in compositional, electronic and/or magnetic fluctuations by the dope of the magnetic iron impurity.

References

1. W. L. JOHNSON, S. J. POON, J. DURAND and P. DUWEZ, *Phys. Rev.* **B18** (1978) 206.
2. T. MASUMOTO, A. INOUE, S. SAKAI, H. M. KIMURA and A. HOSHI, *Trans. Japan Inst. Metals* **21** (1980) 115.
3. T. R. ORLANDO, E. J. MCNIFF JR, S. FORNER and M. R. BEASLEY, *Phys. Rev. B* 19 (1979) 4545.
4. A. INOUE, Y. TAKAHASHI, N. TOYOTA, T. FUKASE and T. MASUMOTO, *J. Mater. Sci.* 18 (1983) 114.
5. Y. B. KIM, C. F. HEMPSTEAD and A. R. STRNAD, *Phys. Rev.* **139** (1965) A-1163.
6. N. R. WERTHAMER, E. HELFAND and P. C. HOHENBERG, *ibid.* **147** (1966) 295.
7. A. A. ABRIKOSOV and L. P. GOR'KOV, *Zh. Eksp. Teor. Fiz.* **39** (1960) 1781; *Sov. Phys. JETP* **12**

(1961) 1243.
8. M. B. MAPLE, W. A. FERTIG, A. C. MOTA, L. E. DELONG, D. WOHLLEBEN, *Solid State Commun.* **11** (1972) 829.
9. C. A. MACDONALD and W. L. JOHNSON, *ibid.* **30** (1979) 775.
10. P. FULDE and K. MAKI, *Phys. Rev.* **141** (1966) 275.
11. N. TOYOTA, A. INOUE, T. FUKASE and T. MASUMOTO, *J. Low-Temp. Phys.* **55** (1984) 393.
12. M. B. MAPLE, *Phys. Lett.* **26A** (1968) 513.
13. M. B. MAPLE and K. S. KIM, *Phys. Rev. Lett.* **23** (1969) 118.

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