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Magnetization measurements of nearly ferromagnetic compounds $\text{TiBe}_{2-x}\text{M}_x$ ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}, \text{Fe}$) in low and high fields

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Résumé. — Nous observons une croissance monotone de la susceptibilité des composés $\text{TiBe}_{2-x}\text{Cu}_x$ avec la concentration du cuivre. Des mesures de l'aimantation à 1,24 K et 4,17 K dans des champs atteignant 213 kOe sont analysées à l'aide du formalisme de Landau des transitions de phase. La concentration critique pour le ferromagnétisme, x_c , est de l'ordre de 0,2. L'introduction des solutés Ag et Au diminue la susceptibilité de TiBe_2 (résultats préliminaires). Dans les composés $\text{TiBe}_{2-x}\text{Fe}_x$ le moment magnétique du fer paraît être inférieur à $0,01 \mu_B$.

Abstract. — It is shown that the substitution of minute amounts of Cu for Be in TiBe_2 causes the susceptibility to increase monotonically. Magnetization data for $\text{TiBe}_{2-x}\text{Cu}_x$ at 1.24 K and 4.17 K in fields up to 213 kOe are analysed in the Landau model of phase transitions. The critical concentration for ferromagnetism, x_c , is about 0.2. Ag and Au as solutes decrease the susceptibility of TiBe_2 (preliminary results). The magnetic moment of Fe in $\text{TiBe}_{2-x}\text{Fe}_x$ is estimated to be smaller than $0.01 \mu_B$.

The magnetic properties of TiBe_2 , the susceptibility of which goes through a maximum for both increasing magnetic field and increasing temperature, are not yet fully elucidated [1]. This cubic (C15) compound has been recently described as an antiferromagnet [2, 3], a metamagnet [4, 5] and — for the time being the prevailing view — as a strongly exchange enhanced paramagnet [6, 7, 8].

Derived compounds such as $\text{TiBe}_{2-x}\text{M}_x$ may also show remarkable properties. A striking feature is the occurrence of ferromagnetism in $\text{TiBe}_{2-x}\text{Cu}_x$ [9, 8, 6, 10, 11] for $x \gtrsim 0.16$ [8]. No detailed theoretical or experimental study of the changes in the electronic structure of TiBe_2 caused by the introduction of Cu is available yet. Moreover, the situation is obscured by the discrepancy between our magnetization data [8, 1] and those of Monod *et al.* and Felner *et al.* [6, 11]. We found in [8] that the low field, low-temperature susceptibility, $\chi(0, 0)$, of $\text{TiBe}_{2-x}\text{Cu}_x$ compounds increases regularly from $x = 0$ through $x = 0.012, 0.05, 0.10$, etc... By contrast the susceptibility reported in [6] and [11] for $x = 0.02$ and $x = 0.03$ is roughly two times smaller than that of TiBe_2 . Thus Felner *et al.* recently reaffirmed that the substitution of minute amounts

of Cu for Be in TiBe_2 causes the susceptibility to go through a minimum [11]. In an attempt to definitely clarify that point we measured the susceptibility of three more $\text{TiBe}_{2-x}\text{Cu}_x$ samples ($x = 0.008, 0.027$ and 0.038). The results are presented here together with partly published data [8] for the same system. Preliminary susceptibility measurements for $\text{TiBe}_{2-x}\text{M}_x$ ($\text{M} = \text{Ag}, \text{Au}, \text{Fe}$) are also included.

Experiments were carried out in the liquid ^4He temperature range with a precision moving sample magnetometer, in fields (H) up to 68 kOe, and with an apparatus of the same type [12], at the National Magnet Laboratory, where fields up to 213 kOe were used. The preparation of the $\text{TiBe}_{2-x}\text{Cu}_x$ compounds (arc-melted and annealed) has been described earlier [9, 10]. The samples with solutes other than Cu were only arc-melted, except for $\text{TiBe}_{1.9}\text{Ag}_{0.1}$ which was also annealed.

Figure 1 shows the variation with concentration of the susceptibility of $\text{TiBe}_{2-x}\text{Cu}_x$ at 4.17 K. We plotted the Landau parameters $A \equiv \chi^{-1} (H \rightarrow 0)$ and B , obtained from Arrott plots of the magnetization (M^2 vs. H/M). As shown in [1] and first suggested in [6], such plots are straight lines for TiBe_2 at helium temperatures, up to magnetic fields of about 40 kOe. The magnetization $M(T, x, H)$ of $\text{TiBe}_{2-x}\text{Cu}_x$ can also be described by the relation $H/M = A(T, x) + B(x) M^2$.

Fig. 1. — Inverse magnetic susceptibility of $\text{TiBe}_{2-x}\text{Cu}_x$ compounds, at 4.2 K, as a function of Cu concentration. Present results are shown by open symbols. Closed symbols are from references [6] and [11]. The data were obtained from Arrott plots (M^2 vs. H/M). Circles correspond to measurements for $0 < H < 40$ kOe and triangles to the highest field range (see text). Insert, variation with concentration of the Landau parameter B .

It is clear from the results for the most dilute samples ($x < 0.03$) that the susceptibility increases regularly with Cu concentration (Fig. 1, open circles). The initial variation of χ^{-1} is given by $\chi^{-1}(x) = \chi^{-1}(0) - \alpha x$, with $\alpha = 1\,330 (\text{emu}/\text{mole})^{-1}$. Also shown, for comparison, are the quite different susceptibility values found by Monod *et al.* [6] and Felner *et al.* [11]. The Landau parameter B (i.e. the inverse slope of the Arrott plots) does also vary smoothly with x (see insert). This initially negative coefficient changes its sign at $x \simeq 0.023$.

The results shown in figure 1 were extracted from figure 2 which shows more explicitly the variation of the magnetization with field, concentration of various solutes and, marginally, temperature. The data points for $\text{TiBe}_{2-x}\text{Cu}_x$ with $x = 0.008, 0.027$ and 0.038 were omitted in figure 2, for clarity.

Fig. 2. — Arrott plots (M^2 vs. H/M) of the magnetization of $\text{TiBe}_{2-x}\text{M}_x$ ($M = \text{Cu}, \text{Ag}, \text{Fe}$) compounds. Open symbols, $T = 1.24$ K. Closed symbols, $T = 4.17$ K. Data for TiBe_2 and $\text{TiBe}_{1.988}\text{Cu}_{0.012}$ extend up to 213 kOe. The straight segment (near $H/M = 100$) represents our detailed measurements [1] for TiBe_2 at 1.45 K. All samples were annealed, except those containing Ag and Fe.

It is seen in figure 2 that the Arrott plots for TiBe_2 at 1.24 K and 4.17 K « turn around » in moderate fields ($45 \lesssim H \lesssim 55$ kOe, see [1] for details) and become nearly rectilinear again at very high fields ($100 < H < 213$ kOe). In that field range B is positive and the corresponding values of A are about two times smaller than the inverse susceptibility in zero field.

The values of χ^{-1} and B obtained from the data in the highest field range are shown in figure 1 by triangles. For $\text{TiBe}_{2-x}\text{Cu}_x$ with $x = 0.05, 0.10$ and 0.16 we determined χ^{-1} and B in the range $40 \leq H \leq 68$ kOe. In spite of this minor inconsistency, a rather smooth variation of the parameters with concentration is found.

From figure 1 it appears that the magnetization of $\text{TiBe}_{2-x}\text{Cu}_x$ with $x > 0.05$ can be described in the whole range of field with a single pair of values for the parameters $A(T, x)$ and $B(x)$ whereas this is not possible for the compounds with a smaller Cu content. Remarkably, only the Landau parameters determined from high field data vary in a simple way when the Cu concentration increases from zero, up to the critical concentration for ferromagnetism, $x_c \simeq 0.2$ (Fig. 1, open triangles).

Obviously, magnetic inhomogeneity in the more concentrated samples gives rise to low field tails in the Arrott plots. It is important to notice that such a tail is not observed in the plots for $x < 0.02$ and becomes barely visible for $x = 0.027$ ($\Delta\chi^{-1}/\chi^{-1} \simeq 2\%$; compare with the larger and larger tails for $x = 0.05$ and 0.10 , in the same range of field, $2 < H < 20$ kOe). This indicates that the increase in χ at low Cu concentration is intrinsic and is not due to the presence of small ferromagnetic regions.

It appears that the two concentrated $\text{TiBe}_{2-x}\text{Cu}_x$ samples ($x = 0.1$ and $x = 0.2$) measured by Monod *et al.* [6] at low temperatures are very inhomogeneous. The Arrott plots, for both samples, have a pronounced low field tail (only M vs. H was shown in reference [6]). In high fields, the magnetization of the $\text{TiBe}_{1.9}\text{Cu}_{0.1}$ sample lies below our curve for TiBe_2 and the latter isotherm practically merges with the data for the $\text{TiBe}_{1.8}\text{Cu}_{0.2}$ specimen. Hence, for $x = 0.2$, the extrapolated χ^{-1} at 4.2 K, which should be nearly zero, is as large as 45 (emu/mole) $^{-1}$ (Fig. 1, closed triangle).

Some more information may be extracted from our data in figure 2.

The high field magnetization curve for $\text{TiBe}_{1.988}\text{Cu}_{0.012}$ at 1.24 K does not merge with that for TiBe_2 at the same temperature. The small relative shift of the Arrott plot for $x = 0.012$ toward the left corresponds to a critical concentration for ferromagnetism $x_c = 0.24$, of the right order of magnitude ⁽¹⁾. This is an additional indication of the quality (homogeneity, nominal concentration) of the samples used ⁽²⁾.

Detailed high field magnetization measurements of TiBe_2 at temperatures up to 20-30 K have not yet been published. The two isotherms of figure 2, at 1.24 K and 4.17 K, show that the temperature variation of M is strongly field dependent (see Ref. [1] for detailed low field data). In zero field χ would increase by 0.8% between 1.24 K and 4.17 K (following initially a T^2 law [1]) while the susceptibility determined by extrapolating the straight high field part of the Arrott plot to $M^2 = 0$, decreases by 10% in the same temperature interval. For $H \simeq 25$ kOe, χ should remain nearly constant between 0 K and 10 K [1]. It would be of interest to determine above which temperature $\chi(H)$ no longer goes through a maximum and to measure the high field values of B at high temperatures, also in $\text{TiBe}_{2-x}\text{Cu}_x$ compounds.

Some of our preliminary data on $\text{TiBe}_{2-x}\text{M}_x$ ($M = \text{Ag, Au, Fe}$) are shown in figure 2. Thinking in terms of electron concentration, one might expect Ag and Au to have qualitatively the same effect as Cu on the magnetic properties of TiBe_2 . This is not found in the present experiments. At 4.17 K the susceptibility of $\text{TiBe}_{1.95}\text{Ag}_{0.05}$ is only 67% of the value for TiBe_2 . This ratio is 56% for $\text{TiBe}_{1.95}\text{Au}_{0.05}$. However these two samples were just arc-melted. For an annealed $\text{TiBe}_{1.9}\text{Ag}_{0.1}$ sample the ratio reaches 86% and the parameter $B \simeq -0.6 \times 10^{-5}$ (emu/mole) $^{-3}$ is still slightly negative. Since Ag and Au have a significantly larger atomic radius than Cu, it is likely that these elements cannot substitute Be in TiBe_2 . Anyway, it seems that we failed in introducing them in the compound, as Felner *et al.* apparently failed in introducing Cu.

As to the $\text{TiBe}_{2-x}\text{Fe}_x$ compounds, our susceptibility results are consistent with those of reference [11]. We find that a Fe concentration of 0.02 (arc-melted sample) decreases the susceptibility by about 4%, which is small. On the other hand, this amount of Fe changes the parameter B from -5×10^{-5} (in TiBe_2) to $+3 \times 10^{-5}$ (emu/mole) $^{-3}$ (see Fig. 2). An even larger increase in B , per unit concentration, is observed for $x = 0.001$. For that sample, $B \simeq -3 \times 10^{-5}$ and the zero field susceptibility is nearly the same as in $\text{TiBe}_{1.98}\text{Fe}_{0.02}$ (within 1%). Hence the initial value of dB/dx is about 5 times larger for $\text{TiBe}_{2-x}\text{Fe}_x$ than for $\text{TiBe}_{2-x}\text{Cu}_x$ (with the same sign). The susceptibility ($1/A$) seems to remain practically unaffected by Fe impurities but increases rapidly with Cu concentration. In band theory, the Landau parameters A and B can be expressed

⁽¹⁾ It is clear from figure 2 that x_c depends on the range of field used. For $H > 100$ kOe, x_c would lie above $x = 0.22$.

⁽²⁾ $\text{TiBe}_{1.95}\text{Cu}_{0.05}$ is an exception. By comparison with the latest samples made ($x = 0.027, 0.038$) we estimate that its magnetization should be larger by a factor 1.08.

in terms of the density, $N(E_F)$, of the electronic states at the Fermi level and its derivatives with respect to energy. From our results we may infer that the introduction of Fe has a strong effect on the fine structure in the density of states, on which B depends, but does not change much $N(E_F)$.

One more clear cut result is that Fe bears no giant moment in TiBe_2 — in fact no moment at all. From the absence, within experimental error, of a tail in the low field Arrott plot for $\text{TiBe}_{1.98}\text{Fe}_{0.02}$ we calculated that the magnetic moment per Fe atom is smaller than $10^{-2} \mu_B$. In that respect TiBe_2 strongly differs from Pd, as noticed in [11].

In conclusion, the present experimental results clearly show that the substitution of Cu for Be in TiBe_2 continuously increases the susceptibility. The complicated way the Landau parameters A and B vary with impurity concentration, magnetic field and temperature (also pressure, see Ref. [13]) still calls for further investigations and interpretations.

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