Superconductivity and Magnetic Aftereffects in the Exchange-Enhanced Paramagnetic Compound TiCo

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Abstract. TiCo, a 3d-band metal, is an exchange-enhanced itinerant paramagnet. We found that polycrystalline Ti$_{0.51}$Co$_{0.49}$ becomes superconducting below approximately 50 mK, and shows typical magnetic aftereffects due to the presence of a small number of ferromagnetic clusters. We studied the relationship between superconductivity and the magnetic aftereffect. The superconducting transition temperature is related to the size and quantity of the ferromagnetic clusters.

Introduction

Shinogi and coworkers [1,2] first reported that CsCl-type TiCo is an exchange-enhanced paramagnet and that the anti-structure Co atoms which occupy some Ti sites have magnetic moments. To avoid this property, Ti$_{0.51}$Co$_{0.49}$ was found to be the best composition. We recently reported that TiCo becomes superconducting below approximately 50 mK.[3,4] The discovery of superconductivity in the nearly ferromagnetic 3d-band itinerant electron system has aroused much interest, because a nearly ferromagnetic material, such as TiCo, may potentially be a novel superconductor as a result of ferromagnetic spin fluctuations. We previously studied the normal state properties and reconfirmed that TiCo is an exchange-enhanced paramagnet.[4] However, we observed abnormal hysteresis in the temperature-dependent susceptibility under low magnetic fields, below approximately 100 Oe. We also observed weak signals that suggested the presence of a small number of ferromagnetic clusters at specific heats below 2.0 K and in the low-field magnetization below 100 Oe. To clarify the origin of these abnormal properties of TiCo, we measured the magnetization relaxation time over the ranges 10–1000 Oe and 7–300 K. The abnormal properties were found to be related to magnetic aftereffects due to a small number of ferromagnetic clusters in the TiCo structure.[5] Furthermore, the superconducting transition temperature was found to be related to the size and quantity of the ferromagnetic clusters.

Experimental

Ti$_{0.51}$Co$_{0.49}$ specimens were prepared by melting weighed quantities of 99.995% Ti and 99.99% Co in an arc furnace. The ingots thus obtained were wrapped in a Ta film, homogenized by annealing in evacuated quartz tubes at 900°C for 100–200 hours, and cooled in the furnace. All surfaces of the ingot samples were cut off to study the sample bulk properties. The samples thus obtained are hereafter referred to as “core samples.” All core samples were homogenized at 900°C for another 100 h, and the thick surfaces of the annealed core samples were polished using emery paper. The magnetization and DC susceptibility were measured using a SQUID magnetometer at temperatures between 1.7 K and 300 K in magnetic fields ranging from 10 Oe to 8000 Oe. The AC susceptibility was measured to detect the Meissner effect of superconductivity at temperatures between 1 K and 10 mK. The earth’s magnetic field was reduced to less than 5 mOe using a mumetal can. The temperatures were measured using a CMN thermometer calibrated with the NBS standard (SRM768) below 1 K.[6] Measurements were carried out on three polycrystalline Ti$_{0.51}$Co$_{0.49}$ core samples: #1, #2, and #3, of the same composition, and prepared in the same way.

Results and Discussions

The temperature dependence of the real part $\chi'$ of the AC susceptibility of the three core samples (#1, #2, and #3) is shown in Fig. 1a, 1b, and 1c, respectively. The samples #1, #2, and #3 showed superconducting transition (onset) temperatures of 50, 30, and 40 mK,
respectively. The differences between their superconducting transition temperatures were quite large. The electrical resistivity, specific heat, and DC susceptibility of samples #1 and #2 were measured in the normal state.[4] These normal-state properties displayed only small differences, with the exception of the low-field DC susceptibility below 100 Oe, which was enhanced and showed abnormal hysteresis in the temperature-dependent curve, suggesting the presence of ferromagnetic clusters.[3,5] Evidence for the presence of ferromagnetic clusters was also observed in the specific heat below 2.0 K.[4] In this letter, the low-field magnetism is described in detail.

Fig. 1. Temperature dependence of the real part $\chi'$ of the AC susceptibility for Ti$_{0.51}$Co$_{0.49}$ core samples. The relations between the amplitudes of the AC magnetic fields and the symbols are shown in (a). The relations are the same for samples (a) #1, (b) #2, and (c) #3.

The origin of the abnormal behaviors described above was revealed by measuring the relaxation time of the susceptibility and magnetization. Figure 2a, 2b, and 2c shows peculiar relaxations in the DC susceptibility $\chi$ of samples #1, #2, and #3, respectively. Here, $\chi$ is defined as the magnetization divided by the magnetic field and mass of the sample. The abscissa is time $t$, in minutes. The relaxation was measured under a magnetic field applied after cooling at zero magnetic field (ZFC). Prior to ZFC, both the sample and superconducting magnet were demagnetized at 300 K. The relaxations at 1000 Oe were very fast, and no differences were observed among the three samples. In contrast, the relaxations at 10 Oe showed marked differences among the samples. We measured the susceptibility over the range 10–8000 Oe. The susceptibility $\chi$ did not change from 1000 to 8000 Oe, and corresponded to the bulk paramagnetic susceptibility of TiCo, the value of which was similar to that measured by Shinogi and coworkers.[1,2] This study examines, in particular, the differences between the susceptibility at 1000 Oe and the susceptibilities at magnetic fields below 1000 Oe (particularly below 100 Oe); that is, deviations from the bulk paramagnetic susceptibility at low magnetic fields.

Application of a magnetic field after ZFC produced susceptibilities at 10 Oe and 100 Oe that approached an initial value within a short period of time. This value is hereafter referred to as the “initial relaxation-1.” Thereafter, the susceptibilities changed very slowly, hereafter referred to as the “long component of relaxation.” Here, the initial relaxation-1 includes both the relaxation of the bulk paramagnetic susceptibility and the initial relaxation-2 of the susceptibility enhancement at a low magnetic field. The initial relaxation-2 is the short-time component of the relaxation of the enhanced susceptibility at a low magnetic field, which is approximately the difference at $t = 0$ between the susceptibility at 1000 Oe and the susceptibility at 10 or 100 Oe. That is, the relaxation of the enhanced susceptibility showed two components, with long and short relaxation times. At 7 K and after ZFC, the DC susceptibility at 10 Oe, after the initial relaxation ($t > 0$), was comparable to that at 100 or 1000 Oe. The DC susceptibilities at 10 Oe of samples #1 and #3 were slightly larger than those at 100 and 1000 Oe, whereas that of sample #2 was slightly smaller than those at 100 and 1000 Oe. The DC susceptibilities at 7 K were almost constant at a time $t$ after the initial relaxation ($t > 0$). This finding indicated that the relaxation time of the long component was so long at 7 K that no
changes could be observed for a very long time of 1200 min. On the other hand, at 200 and 300 K after ZFC, the DC susceptibilities of all three samples at 10 Oe after the initial relaxation ($t > 0$) were large compared with those at 100 and 1000 Oe. In addition, at these temperatures, the DC susceptibility at 10 Oe was not saturated, even after 1200 min. This finding indicated that the relaxation times of the long component at 200 and 300 K were very long, but shorter than the relaxation times at 7 K. After demagnetization at 300 K, the DC susceptibilities of samples #1 and #2 were also measured at 10 Oe with decreasing temperature under the magnetic field, that is, with “field cooling, FC at 10 Oe”. These measurements are shown in Fig. 2a and 2b as double circles on the line $t = 0$. At 7 and 200 K, the DC susceptibility at 10 Oe after FC was much larger than the susceptibilities after ZFC.

The long components of the relaxation times at 200 and 300 K in Fig. 2a and 2b after the initial relaxation were fitted to single exponential functions using the least squares method. However, the fits were not satisfactory. The obtained relaxation times were on the order of 100 h, and the time dependences were not accurately modeled by the single exponential functions. Therefore, we plotted the data against the logarithm of time. $\chi$ showed a linear dependence with respect to $\log t$ over a wide range of time scales. Thus, the extra susceptibility and magnetization that appeared at low magnetic fields may be summarized as follows: (1) the smaller the magnetic field, the longer the relaxation time; (2) the lower the temperature, the longer the relaxation time; (3) the short relaxation time component (i.e., the initial relaxation-2) appeared immediately after applying or excluding the magnetic field; (4) the long relaxation time component of the susceptibility or magnetization, which was observed after the initial relaxation, was very long and showed a linear dependence on $\log t$; and (5) the hysteresis between ZFC and FC was a result of this extremely long relaxation time.

What is the origin of the extremely long relaxation time of magnetization with the

![Figs. 2. Relaxation of the DC susceptibility of Ti_{0.51}Co_{0.49} core samples under an applied magnetic field after ZFC. The data denoted by the double circles were measured after FC. Shown are data for samples (a) #1, (b) #2, and (c) #3.](image)
above-mentioned characteristics (1)–(5)? The observed behavior was consistent with typical magnetic aftereffects originating from small ferromagnetic clusters (single domains) in a magnetically ordered state. A magnetic aftereffect is a phenomenon in which magnetization is delayed upon application of a change in the magnetic field. Chikazumi et al. showed that the relaxation time of thermally fluctuating aftereffects, caused by thermal fluctuations in the magnetization of small ferromagnetic clusters, is a function of temperature, magnetic field, and volume of the ferromagnetic clusters.[7] The relaxation time increased with decreasing temperature and magnetic field, and with increasing ferromagnetic cluster volume. Here, the volume corresponded to the magnitude of the magnetic moment of the single domain cluster in the magnetically ordered state. The relaxation time became extraordinarily long when the cluster volume was larger than a critical value, at which point magnetic aftereffects were observed. It should be noted that the cluster showed a well-known super-paramagnetism when the cluster volume was smaller than the critical value. The critical value of the cluster volume depends on the anisotropic energy and may be roughly estimated, as a typical example, to be on the order of $10^{-20}$ cm$^3$ (the diameter of a spherical cluster is approximately $30 \, \text{Å}$). Therefore, if the cluster size is distributed over a certain range around a critical value, the relaxation times should be distributed over an extremely wide range of several orders of magnitude. In such a case, the relaxation would depend linearly on the logarithm of time.

As mentioned above, the anti-structured Co occupying Ti sites has a magnetic moment. Therefore, a small number of ferromagnetic clusters may appear within bulk TiCo. The magnetic moments of these clusters may be enhanced by neighboring itinerant electrons, similar to the well-known giant moments in Pd metals containing magnetic impurities. A small number of magnetic impurities, such as iron, may be present in the sample and may form ferromagnetic clusters. Thus, the extremely long relaxation time of the magnetization is most likely attributed to ferromagnetic clusters in TiCo, the sizes of which are near the critical value. The Curie temperature for ferromagnetic ordering of these clusters exceeds 300 K.

Figure 2a, 2b, and 2c shows that the susceptibility of sample #2, at 10 Oe and 300 K after ZFC, was considerably larger than the susceptibilities of samples #1 and #3. The susceptibilities of sample #2 at the three temperatures after FC were considerably larger than those of sample #1. These results indicate that the number of ferromagnetic clusters was larger in sample #2 than in samples #1 and #3. On the other hand, the susceptibility of sample #2, at 10 Oe and 7 K after ZFC, was smaller than the susceptibilities of samples #1 and #3. This finding indicated that the relaxation time of the initial relaxation-2 at 7 K was longer in sample #2 than in samples #1 and #3, and that the size of the ferromagnetic clusters was larger in sample #2 than in samples #1 and #3. These factors may explain why the superconducting transition temperature of sample #2 was lower than that of samples #1 and #3. Considering that the cluster size and number may be changed according to the sample preparation and annealing conditions, the considerable sample dependence of the superconducting transition temperature for TiCo, as mentioned above, may be caused by these ferromagnetic clusters.

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