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Substitute effects of Ga on T_c in superconducting $Zr_2(Co_{1-x}Ga_x)$

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ABSTRACT

As revealed in the powder X-ray diffraction and crystallographic data, the body-centered tetragonal structure of the parent compound Zr_2Co is retained in $Zr_2(Co_{1-x}Ga_x)$ up to the solubility limit near $x = 0.3$. Variation of room temperature lattice parameters indicates that parameter a increases linearly with increasing x up to $x = 0.2$ then saturates while c and c/a values decrease linearly with x up to $x = 0.3$ due to doping with Ga. A prominent maximum in the unit cell volume v versus x curve therefore appears around $x = 0.2$. Magnetic and electrical measurements show that there is an explicit maximum T_c close to $x = 0.05$. This demonstrates that the superconducting transition temperature of the pseudo-binary system $Zr_2(Co_{1-x}Ga_x)$ is not a monotonic function of the lattice constants a, c, c/a, or v. As compared with the $Zr_2(Co_{1-x}Ni_x)$ system, it is suggested that the superconducting transition temperature in $Zr_2(Co_{1-x}Ga_x)$ may relate more to the spin density fluctuations than to the density of states at the Fermi level.

1. Introduction

The superconducting phase diagram of $Zr_2(Co_{1-x}Ni_x)$, as reported by Kakutani et al. [1], shows that there is an explicit maximum T_c close to $x = 0.1$. This demonstrates that the superconducting transition temperature is not a monotonic function of the Ni substitution x irrespective of the same valences of Co and Ni. It may be suggested that the electronic structures of this class compounds should depend on more than just the valence electron density and the lattice parameters if the conventional BCS (Bardeen, Cooper, Schrieffer) theory [2] does not fail. However, Takekuni et al. [3] used the nuclear-magnetic-resonance (NMR) method to study ^{59}Co in the normal state of $Zr_2(Co_{1-x}Ni_x)$ and to investigate the itinerant nearly antiferromagnetic behavior in superconducting $Zr_2(Co_{1-x}Ni_x)$. Very interestingly, they found that the superconducting transition temperature related more to the spin density fluctuations around $q = Q$ (Q being an AF wave vector) than to the density of states at the Fermi level. Since Zr_2Ga, as well as Zr_2Co, crystallizes in the Al_2Cu-type tetragonal structure with space group $I_{4/mcm}$ [4], an isostructural pseudo-binary series $Zr_2(Co_{1-x}Ga_x)$ is expected to be formed. We had hopes that this system would provide an excellent opportunity to explore the effects of alloying as well as the extensive examination on the theory of superconductivity.

2. Experimental

Polycrystalline samples investigated for this work were prepared by arc melting proper amounts of the elements on a water-cooled Cu hearth in 1 atm of ultra-high-purity argon gas in which a Zr button used as an oxygen getter had been previously arc melted. The 99.8% purity Zr, 99.9+ purity Co and 99.9999% purity Ga were purchased from Alfa Aesa, A Johnson Matthey Company. Fourteen samples with different compositions in the series $Zr_2(Co_{1-x}Ga_x)$ ($0 \leqq x \leqq 1.0$) have been made. Weight losses (<0.06%) during arc melting were negligible. Referring to the Zr–Co phase diagram [5], each arc-melted sample was sealed under argon in a quartz tube and annealed for 5 days at 820 °C to ensure the sample's homogeneity. This heat treatment was followed by a water quench to room temperature. A microcomputer controlled MXP3 diffractometer equipped with copper target and graphite monochrometer for CuK_α radiation was used to get powder X-ray diffraction patterns. The lattice parameters of the unit cell were determined by using PowderCell program [6]. The static magnetic susceptibility measurements were carried out with a commercial SQUID (Superconducting QUantum Interference Device) magnetometer [7] in which the sample was moved slowly through the pickup coil. Electrical resistivity measurements (dc) were made using a standard four-probe technique in a system fully automated for temperature stability and data acquisition [7]. Fine platinum wires (~2 mil diameter) were spot-welded to the sample and served as the voltage and current leads. Data were taken with the current (10 mA) applied in both directions to eliminate possible thermoelectric effects. A Keithley Model 220 was taken as a constant current source

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and a Keithley Model 182 nanovoltmeter was used to measure the output voltage. The midpoint of the transition will be taken as the superconducting transition temperature $T_{c,\mathrm{mid}}$ and the transition width will be taken as 10%–90% values for both magnetic and electrical measurements. As to the $T_{c,\mathrm{onset}}$, the point will be taken as the interaction of the normal state line and the superconducting transition line.

3. Results and discussion

The observed powder X-ray diffraction patterns at room temperature for five representative samples in the series $Zr_2(Co_{1-x}Ga_x)$ with $x = 0$, 0.1, 0.2, 0.3, and 0.4 are shown in Fig. 1(a)–(e). It is found that the structure of the parent compound Zr_2Co is retained in $Zr_2(Co_{1-x}Ga_x)$ up to the solubility near $x = 0.3$. The sharp and indexed peaks of the observed pattern confirm that these compounds crystallize in a tetragonal structure with space group $I_{4/\mathrm{mcm}}$. However, for the samples with $x > 0.3$, there are additional peak lines marked $*$, as shown in Fig. 1(e), due to the impurity phase of Zr_5Ga_3. It is not unexpected that the extensive solid solutions cannot be fully completed in $Zr_2(Co_{1-x}Ga_x)$ though the compound Zr_2Ga has the same crystal structure as Zr_2Co because of the stable phase of Zr_5Ga_3 as manifested in the Zr–Ga phase diagram [8]. The refined lattice parameters a, c and the c/a values, determined by the PowderCell program, are listed in Table 1 and replotted as a function of Ga concentration in Fig. 2(a)–(c). It is surprising that the crystallographic parameter a increases linearly with increasing x up to $x = 0.2$ then saturates while c and c/a value decrease linearly with x up to $x = 0.3$ due to a large percentage change for c rather than a. A prominent maximum in the unit cell volume v versus x curve therefore appears around $x = 0.2$, as shown in Fig. 2(d). Obviously, there is not a simple trend. Though the origin of these anomalies observed in $Zr_2(Co_{1-x}Ga_x)$ is not clearly known at present, it is expected that this abnormal phenomenon may also be reflected in the intrinsic electronic structure. It should be understood in a more strict sense that there is still some extent of inhomogeneity in the samples with x small less than 0.3. For comparison, it is noticeable that, contrary to the $Zr_2(Co_{1-x}Ga_x)$ system, there is an overall tendency for c to increase and for a to decrease with increasing x in the $Sr(Ga_xSi_{2-x})$ [9] or $Ca(Al_{1-x}Ga_x)Si$ [10] system.

Fig. 3(a) and (b) present the temperature dependence of the zero-field cooled (ZFC) and field-cooled (FC) magnetization for seven samples in the system $Zr_2(Co_{1-x}Ga_x)$ ($x = 0$, 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3) measured in a field of 10 Oe between 2.0 and 7.0 K. All measurements were executed on bulk samples of about 0.2 g mass. For each sample, the ZFC curve shows a sharp transition and reaches saturation at a lower temperature, which is an indication of the superconducting phase homogeneity in the sample. Different magnetization data appearing at low temperatures for each sample can be explained in terms of the sample's irregular shape and its corresponding geometrical demagnetization factor. The reduced Meissner flux expulsion from FC data is a feature of the flux trapping effect in the compound. It is noted that the shielding curves for constant field shift toward the higher temperature region with increasing Ga concentration up to x around 0.05 than backward to a lower temperature area. The superconducting transition temperature $T_{c,\mathrm{mid}}$ and $T_{c,\mathrm{onset}}$ data thus obtained in the series $Zr_2(Co_{1-x}Ga_x)$ ($0 \leqq x \leqq 0.3$) are reported in Table 1.

Though electrical measurements are vulnerable to small amounts of a superconducting minor phase which could form a continuous network at grain boundaries leading to zero resistance, the resistivity data normalized at 8.0 K for seven samples in $Zr_2(Co_{1-x}Ga_x)$ ($x = 0$, 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3) are depicted in Fig. 4(a) and (b). It is found that the superconducting transition temperatures as determined by either electrical or magnetic

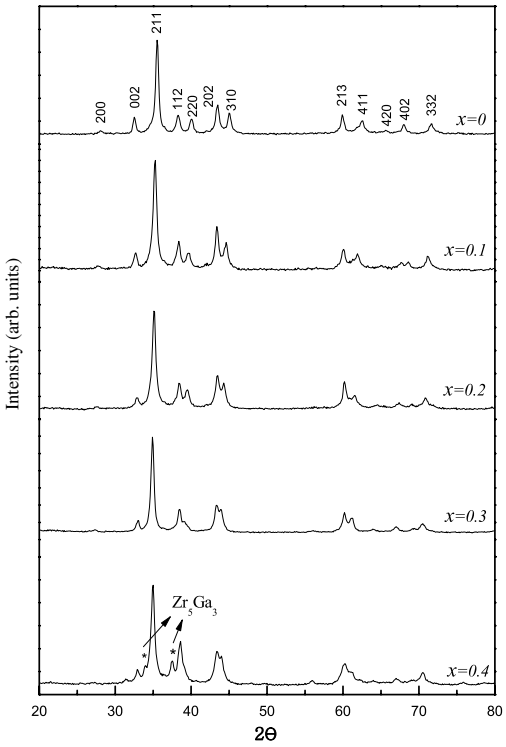

Fig. 1. Powder X-ray diffraction patterns at room temperature for five representative samples in the series $Zr_2(Co_{1-x}Ga_x)$ with $x = 0$, 0.1, 0.2, 0.3, and 0.4.

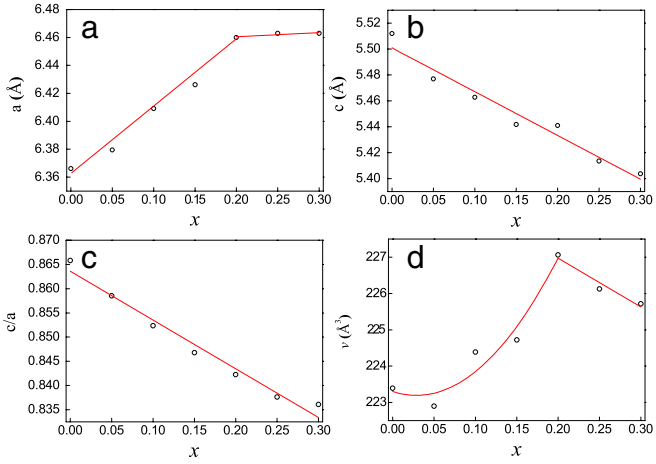

Fig. 2. Variation of lattice parameters versus Ga concentration x in $Zr_2(Co_{1-x}Ga_x)$: (a) a versus x, (b) c versus x, (c) c/a versus x and (d) v versus x.

method are well consistent in spite of the fact that the zero resistivity temperature is slightly higher than the transition point value obtained by magnetization measurements. This slight variation in T_c may be due to the different effective time scales involved in magnetic and electrical measurements. The possible surface superconductivity [11,12] of these intermetallic compounds is also not excluded.

The critical temperatures $T_{c,\mathrm{mid}}$ as established by above two types of experiments (χ_{dc} and ρ) are plotted as a function of Ga content x in Fig. 5. The salient feature of the $T_{c,\mathrm{mid}}$ vs. x curve is the presence of one peak around $x = 0.05$. Experience may tell us that for an electron–phonon weakly coupled superconductor, e.g., LaNiSi [13], its pseudo-ternary system $La(Pt_{1-x}Ni_x)Si$ exhibits monotonic T_c functions of x [14]. As expected, the variation of the lattice parameters in $La(Pt_{1-x}Ni_x)Si$ also obeys Vegard's law [14]. It looks like the rigid band model is not sufficient to account for