Decoupling of itinerant and localized d-orbital electrons in the compound Sc$_{0.5}$Zr$_{0.5}$Co

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Abstract
By using the arc-melting method, we successfully synthesize the compound Sc$_{0.5}$Zr$_{0.5}$Co with the space group of Pm$-3m$. Both the resistivity and magnetic susceptibility measurements reveal a phase transition at about 86 K. This transition might be attributed to the establishment of an antiferromagnetic order. The magnetization hysteresis loop measurements in wide temperature region show a weak ferromagnetic feature, which suggests a possible canted arrangement of the magnetic moments. Bounded by the phase transition temperature, the resistivity at ambient pressure shows a change from Fermi liquid behavior to a super-linear behavior as temperature increases. By applying pressure up to 32.1 GPa, the transition temperature does not show a clear change and no superconductivity is observed above 2 K. The density functional theory calculations simulate the antiferromagnetic order and reveal a gap between the spin-up and spin-down d-orbital electrons. This kind of behavior may suggest that the antiferromagnetic order in this compound originates from the localized d-electrons which do not contribute to the electric conduction. Thus the itinerant and localized d-orbital electrons in the compound are decoupled.

Keywords: itinerant and localized, antiferromagnetic order, the DFT calculations

(Some figures may appear in colour only in the online journal)

1. Introduction
Since the discovery of cuprates [1] and iron based superconductors [2], antiferromagnetic spin fluctuations are assumed to be the possible superconducting pairing glue, which leads to the unconventional superconductivity [3]. And the emergence of superconductivity accompanied by the suppression of long-range antiferromagnetic order becomes one of the common features of unconventional superconductors, such as cuprates, iron based superconductors, and CrAs [1, 4, 5]. It has been known that, for CrAs and some iron based parent compounds like LaFeAsO and BaFe$_2$As$_2$ high pressure is an effective and clean way to suppress the antiferromagnetic order and induce superconductivity [5–7]. However, high pressure is not always effective in bringing in superconductivity for some compounds with the antiferromagnetic order originated from localized d-electrons, such as NiO [8], and Cr$_2$GaN [9]. For this kind of compounds, it is very hard to suppress the antiferromagnetic order solely by external pressure.
Nowadays, alloys containing cobalt have attracted much attention, because these compounds sometimes show novel physical properties which are related to the correlation effect generated from 3d-electrons of cobalt. For example, the cobalt based Heusler alloy Co$_2$MnSi exhibits a huge spin polarization, and Co$_2$CrAl reveals a temperature-dependent anomalous Hall effect [10–12]. The compound Zr$_2$Co was reported as a superconductor with an itinerant antiferromagnetism in the normal state revealed by the NMR study [13, 14]. Meanwhile, ScZrCo alloy crystallized in the Ti$_2$Ni structure, was reported as a correlated bad metal and could become a superconductor by the high pressure tuning [15].

Here, we report the successful synthesis and characterization of the compound Sc$_{0.5}$Zr$_{0.5}$Co. Multiple experiment tools reveal that the system may have an antiferromagnetic transition at about 86 K, and the phase transition seems to be quite robust under high pressures. Only in the low pressure region, for example below 3.1 GPa, there is a slight suppression of the antiferromagnetic transition temperature from 86 K at ambient pressure to 74.3 K under 3.1 GPa. However, with further increasing pressure, the antiferromagnetic transition temperature becomes unchangeable and no superconductivity is observed above 2 K. This feature probably indicates that the localized d-electrons, which are not involved in electronic conduction, are the cause for the antiferromagnetic order in Sc$_{0.5}$Zr$_{0.5}$Co. The density functional theory (DFT) calculations simulate the antiferromagnetic order and there is a huge gap between the band of the spin-up and spin-down d-orbital electrons originated from the Co atoms along the X–W line, which means spin-flip can hardly happen with applying external magnetic field.

2. Experimental methods

By using the arc-melting method, we fabricated the polycrystalline samples of Sc$_{0.5}$Zr$_{0.5}$Co. Firstly, the scandium (Aladdin, ingot, purity 99.9%) and zirconium (Aladdin, slug, purity 99.5%) were crashed and grounded into powders. Then, the scandium, zirconium and cobalt powders (Alfa Aesar, powders, purity 99.99%) with the mole ratio of 1:1:2 were weighed, ground carefully and pressed into a pellet in a glovebox filled with argon. Afterwards, the pellet was melted in a copper base arc-melting furnace. During the arc-melting process, the chamber was evacuated first and then it was filled with Ar gas. To improve the homogeneity of samples, each pellet was remelted at least four times. The mass loss after arc-melting was about 1.3%.

The x-ray-diffraction (XRD) measurements were carried out on a Bruker D8 Advanced diffractometer with the CuK$_{α1}$ radiation and the wavelength of CuK$_{α1}$ radiation is 1.54056 Å. The energy dispersive spectrums were obtained with a Phenom ProX scanning electron microscope (SEM) at an accelerating voltage of 15 kV. The resistivity at ambient pressure was measured with the standard four-probe method on a Physical Property Measurement System (PPMS, Quantum Design). The DC magnetization measurements were performed on an SQUID-VSM (Quantum Design). The resistivity data under high pressure were collected by using a diamond-anvil-cell (DAC) module which matches our PPMS (cryoDAC-PPMS, AlmánexyLab) equipment with a four-probe van der Pauw method [16]. The applied pressures were determined by measuring the shift of ruby $R_1$ luminescent line [17].

The DFT calculations were performed by the WIEN2k package [18], which utilizes the full-potential linearized augmented plane-wave in contrast to the pseudo-potential method. The Perdew–Burke–Ernzerhof (PBE) exchange correlation energy was implemented to carry out the self-consistent field cycle. The convergence criteria were $10^{-4}$ Ry for energy and $10^{-3}$ e for charge.

3. Experimental methods

3.1. Sample characterization

Figure 1(a) presents the XRD pattern (symbols) for the Sc$_{0.5}$Zr$_{0.5}$Co polycrystalline sample measured at room temperature. The inset shows the schematic structure of Sc$_{0.5}$Zr$_{0.5}$Co. (b) EDS line scan on SEM image and the content ratio of Co, Zr and Sc.

![Figure 1](image-url)
Table 1. Crystallographic data of Sc$_{0.5}$Zr$_{0.5}$Co at 300 K.

| Compound | Sc$_{0.5}$Zr$_{0.5}$Co |
|----------|-----------------------|
| Space group | Pm$\overline{3}$m |
| $a$ (Å) | 3.178(5) |
| $V$ (Å$^3$) | 32.112(1) |
| $\rho$ (g cm$^{-3}$) | 6.568 |
| $R_w$ (%) | 2.47 |
| $R_p$ (%) | 1.95 |
| GOF | 1.06 |

| Atom | Site | $x$ | $y$ | $z$ | Occupancy | $B_{eq}$ |
|------|------|-----|-----|-----|-----------|---------|
| Co   | 1b   | 0.5 | 0.5 | 0.5 | 1         | 1.464   |
| Sc   | 1a   | 0   | 0   | 0   | 0.5      | 0.1325  |
| Zr   | 1a   | 0   | 0   | 0   | 0.5      | 0.8759  |

spectroscopy (EDS), which is in figure 1(b). As we can see, the ratio of the three elements is very uniform with Sc:Zr:Co = 1:0.97:2.08, which is close to the nominal compositions.

3.2. Transport and magnetic properties

Figure 2(a) shows the temperature dependence of resistivity for Sc$_{0.5}$Zr$_{0.5}$Co at ambient pressure. As we can see, a clear anomalous kink occurs at about 86 K indicating a possible phase transition. Above this temperature, the resistivity shows a linear behavior with the resistance temperature coefficient of about 0.0878 $\mu\Omega$ cm K$^{-1}$. However, below the phase transition temperature, the resistivity curve reveals a quadratic relation, which is the typical feature of a Fermi liquid behavior. In figure 2(b), we present zero-field cooled (ZFC) and field cooled (FC) DC magnetization for Sc$_{0.5}$Zr$_{0.5}$Co sample under several magnetic fields. A kink at the same temperature shown in the resistivity is also detected. Around 86 K, the magnetic susceptibility data reveals a clear signature of phase transition, however the data above 86 K do not obey the Curie–Weiss Law. The maximum of magnetic susceptibility with external field of 10 kOe is about $3.1 \times 10^{-3}$ emu cm$^{-3}$ Oe$^{-1}$, which is much smaller than that in normal ferromagnetic materials (about $1-10^5$ emu cm$^{-3}$ Oe$^{-1}$). Thus, the phase transition behavior is very similar to some antiferromagnetic compounds like TiAu, BaFe$_2$As$_2$, etc [21, 22]. Thus, the phase transition at 86 K probably corresponds to an antiferromagnetic transition. And if it is an antiferromagnetic ordering temperature, the Néel temperature does not change when we increase the magnetic fields up to 7 kOe. Besides these, in the low temperature region below 15 K at 10 kOe, $\chi_{DC}(T)$ shows a deviation between the ZFC and FC curves, which indicates a hysteresis of magnetization and may suggest a spin-glass-like behavior.

The magnetization hysteresis loop (MHL) measurements at different temperatures shown in figure 3 exhibit a weak ferromagnetic feature. And the feature does not change disregard the temperature is above or below the Néel temperature, which means that if it was a ferromagnetic phase, the transition temperature would be higher than 150 K. Thus the transition at 86 K should not be a ferromagnetic transition. It may suggest that the magnetic moments of Sc$_{0.5}$Zr$_{0.5}$Co have a canted feature leading to the weak ferromagnetism. The coercive magnetic field $H_C$ and remanent magnetization $M_r$ are detailed in the inset of figure 3. Because the antiferromagnetic order is mainly caused by the neighboring Co atoms with opposite spins, some vacancies of Co atoms or the unavoidable mutual doping of three kinds of atoms are thought to be responsible for the weak ferromagnetic feature. However, we cannot rule out the possibility that the weak ferromagnetic moment comes from the effect of magnetic impurities, which cannot be detected by the XRD measurements.

Figures 4(a) and (b) display the temperature dependence of resistance for Sc$_{0.5}$Zr$_{0.5}$Co under different external pressures, and no superconductivity is observed up to 32.1 GPa above
In the beginning, as increasing the pressures, the resistance of the sample decreases until 12.2 GPa, together with the enlarged residual resistance ratio (RRR). With further increasing pressure, the resistance gets enhanced slowly, while the RRR slightly decreases. In order to determine the phase transition temperature more accurately, we take the derivative of resistance with respect to temperature and show the results in figures 4(c) and (d). The anomalies of the \( \frac{dR}{dT} \) curves as marked here represent the antiferromagnetic transition. We take the temperatures of kinks as the Néel temperatures. Below 3.1 GPa, the Néel temperature slowly decreases with increasing pressure, as shown in the inset of Figure 4(c), it changes from 86 K at ambient pressure to 74.3 K at 3.1 GPa. However, when we keep increasing the pressure, as shown in figure 4(d), the Néel temperature does not change and remains at 74.3 K. These indicate that the antiferromagnetic order is very robust and the response to pressure is very weak in Sc_{0.5}Zr_{0.5}Co.

As we can see from figures 4(a) and (b), the conductance which is attributed by itinerant electrons can be easily tuned by pressure. Thus, the electrons attributing to the antiferromagnetic order should be localized. In other words, the itinerant d-orbital electrons contributing to the conductance are decoupled with the localized d-electrons which is responsible for the antiferromagnetic order. Therefore, this may be the reason why we cannot suppress the antiferromagnetic order and obtain possible superconductivity in this compound.

Figure 5 shows the fitting results to the resistance curves by using the formula \( R = R_0 + A T^2 \) under different pressures. As we can see, under all pressures, the resistance can be well fitted by the formula with a quadratic temperature dependence, which indicates that the system shows a persistent Fermi liquid behavior at all pressures. As shown in the inset of figure 5, the fitting parameter \( A \) shows a linear change from 1.7 GPa to 7.0 GPa with a rate of \(-6.754 \text{n}\Omega\text{K}^{-2}\text{GPa}^{-1}\). While, above 12.2 GPa, \( A \) remains basically unchanged. This is consistent with the response of the conductance to the pressure. Below 12.2 GPa, conductivity enhances with increasing pressure. Further increasing pressure, the conductivity is weakly affected by pressure.

### 3.3. Ab initio calculations and discussions

In order to have a comprehensive understanding to the data obtained in this experiment, we have conducted ab initio DFT calculations. We think the antiferromagnetic order probably comes from the Co atoms and divide the neighboring Co atoms into two parts: Co1 atoms and Co2 atoms and their magnetic moment are arranged in antiferromagnetic order. The initial lattice parameters are taken from our experimental measurements. To present this magnetic order, a \( 2 \times 2 \times 2 \) supercell with a space-group \( Fm \#216 \) is adopted, which also gives a formal stoichiometry. We also performed an optimization for the lattice parameters of the supercell, while the atomic positions are fixed by the symmetry. We can see from figure 6(a) that Co1 and its nearest Co2 form an antiferromagnetic order. Based on this assumed AF model, we have accomplished the calculation about the band structure and the density of states (DOS) diagram which are shown in figure 6. We can see that the DOS for both up spin and down spin are almost identical. Also, the spin magnetic moment is 0.304 \( \mu_B \) per Co1 atom and \(-0.304 \mu_B \) per Co2 atom. A closer scrutinizing to band structures along the X–W line, the fat bands near the Fermi energy consist of localized \( e_g \)-orbital electrons of Co atoms. And there is a clear gap about 0.34 eV between the up spins and down spins, which should be responsible for the robust antiferromagnetic properties we observed in experiments. Meanwhile, some itinerant \( e_g \)-orbital electrons of Co atoms form a hole pocket at \( L \) point, and they are the main part of the itinerant electrons contributing to the electric conductivity. Therefore it is clear that the electrons from different sub-orbits play different roles.
Figure 6. (a) The AF structure of spins of Co atoms. (b) Total and orbital projected DOS of Sc0.5Zr0.5Co. Band Structure of Sc0.5Zr0.5Co for (c) spin up and (d) spin down. The size of the symbols represents the weight of $\varepsilon_g$-orbital electrons of Co1 atoms.

Some are localized and responsible for the formation of magnetic moment, while the other are itinerant leading to the electric conduction. In the transition metal compounds, the balance between the localization and itineracy of the d-electrons is very essential to determine the intrinsic properties of the materials. Note that the energy of the AF configuration we consider here is very close to that of the FM configuration. Specifically, the energy of the FM configuration is 1.53 mRy/atom lower than the AF one. This energy difference between the FM and AF configurations in present system is however much smaller than that in FeCr and FeCo [23]. Despite a little higher energy of the AF order in the calculations, experimentally we find that the AF order may exist below 86 K. This discrepancy may be attributed to some factors which have not been considered in the calculations, for example, the possible random arrangement of Zr and Sc, and off stoichiometry of three kinds of atoms in the formula.

4. Conclusion

In conclusion, we have successfully synthesized Sc0.5Zr0.5Co by arc-melting method. The magnetization and resistivity data indicate a possible antiferromagnetic transition at 86 K, although a weak ferromagnetic signal is detected in the temperature regions both below and above 86 K. By applying external pressures, the electric conduction of the sample is significantly affected, but the antiferromagnetic transition temperature responses weakly. Our DFT calculations indicate that the d-electrons of Co atoms split into itinerant part and localized part. The itinerant part is responsible for the conductivity of the compound, while the localized part gives rise to the antiferromagnetism we observed in experiments. Besides, we can see from the band structures that there is a clear gap between the up and down spins, which indicates a strong antiferromagnetism and is consistent with our magnetization measurements.

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