The First Binary Compound of Cobalt with Bismuth

Sophie Tencé, Cornelius Krellner, Susann Leipe, Ulrich Schwarz, Yuri Grin, and Frank Steglich

Many binary intermetallic compounds containing bismuth and transition metals (*TM*) exhibit superconducting properties which makes the study of such systems attractive. For example, the Ni-Bi and Rh-Bi phase diagrams have been widely explored and highlight the existence of the superconductors $NiBi_3$ (T_c = 4.0 K), NiBi (T_c = 4.25 K), $RhBi_4$ (T_c = 2.8 K) or Rh_3Bi_{14} (T_c = 3.15 K) [1–4]. In particular, those materials are of interest in which the *TM* might retain magnetic providing the possibility of unconventional superconductivity at the border of magnetism. However, for some combinations of Bi and transition metals binary compounds were not reported hitherto [5, 6]. As one example, in the Co-Bi system only a large immiscibility in the liquid state was observed at ambient conditions. This opens the possibility to discover new materials by using different routes of synthesis. Moreover, it is interesting to notice that the coexistence of superconductivity with ferromagnetic order was reported very recently in $NiBi_3$ nanostructures [7]

The goal of the present project is to re-investigate some *TM*-Bi phase diagrams in a quest for new superconductors. Here, we report our first results concerning the Co-Bi system. While it is simple to grow Bi-rich single crystals in the binary systems Ni-Bi or Rh-Bi utilizing a Bi-flux method for example, Co-Bi phases cannot be obtained by such a method. Also, conventional heat treatments failed to synthesize cobalt and bismuth binaries because of the immiscibility gap [5, 6].

$CoBi_3$: Synthesis and Chemical Characterization

We succeeded to synthesize the first binary Co-Bi compound using a high-pressure, high-temperature technique. Powders of bismuth (99.999 %, 100 µm mesh) and cobalt (99.99 %, 200 mesh) were carefully mixed by ball-milling inside a glove box with the molar ratio Bi:Co = 3:1. High pressure was applied by means of an octahedral multi-anvil press, with a boron nitride crucible as the reaction vessel [8]. The samples were exposed to pressures of 5 GPa or 10 GPa for several hours and at temperatures between 370 °C and 1200 °C. They were finally cooled to room temperature before releasing the pressure. The sample containing the highest content of the new phase (85 at.%) is obtained by applying a pressure of 5 GPa at 450 °C for a period of 2 days.

The peaks of the X-rays powder diffraction (XRD) pattern are well indexed with the orthorhombic space group *Pnma* with the unit cell parameters a = 8.8464(7) Å, b = 4.0697(4) Å and c = 11.5604(9) Å. The diffraction data suggest that the new phase has the composition $CoBi_3$ and is isostructural to $NiBi_3$ and $RhBi_3$ [4, 9]. This result is confirmed by electron-probe analysis with wavelength-dispersive X-ray spectroscopy (WDXS) which yields $Co_{24.5(3)}Bi_{75.5(3)}$ as the chemical composition. Thus, $CoBi_3$ crystallizes with the orthorhombic $RhBi_3$-type structure (space group *Pnma*, no. 62) which is depicted in Figure 1. In this anisotropic structure, the bismuth atoms form mono-capped trigonal prisms Bi_7 which are connected to each other by sharing the non-capped square faces. In this way, columns along the [010] axis are built up. The cobalt atoms are inserted in these capped trigonal prisms [$CoBi_7$] and form a zigzag chain along [010], with a zigzag angle of 99.7° and a Co-Co distance of 2.66 Å.

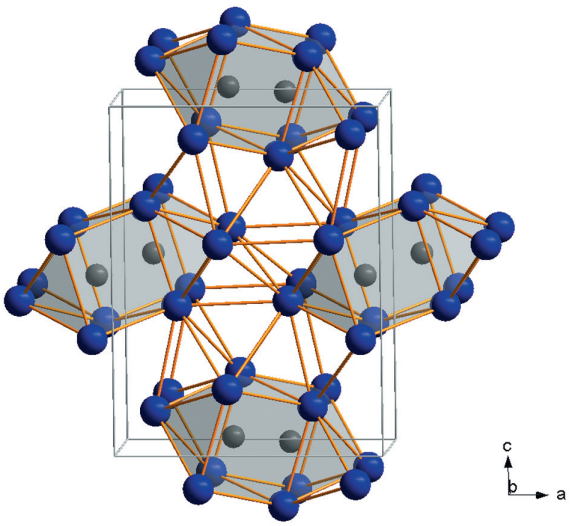

Fig. 1: Crystal structure of $CoBi_3$. The capped trigonal prisms of bismuth atoms (in blue) form chains along the b axis and contain the cobalt atoms (in gray).

We observe a slight anisotropic compression of the unit cell volume $V = 416.2$ Å^3 in comparison to $NiBi_3$ ($a = 8.880$ Å, $b = 4.100$ Å, $c = 11.478$ Å and $V = 417.8$ Å^3 [9]) since the lattice parameters a and b decrease (– 0.4 % and – 0.7 %) whereas c increases (+ 0.7 %).

The Differential Scanning Calorimetry (DSC) measurement displays a small exothermic minimum at about 230 °C and a sharp endothermic peak at 270 °C upon heating the sample. The two anomalies correspond to the decomposition of $CoBi_3$ and the melting of pure bismuth, respectively. Subsequent cooling does not reveal an anomaly at 230 °C any more, and the XRD measurements performed at room temperature on the DSC products exhibit solely reflections of elemental Bi and Co. These two observations manifest the metastable character of $CoBi_3$.

Resistivity and Specific Heat Measurements

The electrical resistivity $\rho(T)$ of the polycrystalline sample $CoBi_3$ was measured between 0.33 K and 300 K by an a.c. four-point method utilizing a Quantum Design PPMS with a ^{3}He insert. The temperature dependence of ρ exhibits a metallic character but with large values at room temperature (800 μΩcm) that most probably result from grain boundary scattering. The presence of remaining Bi and Co in the sample explains the low residual resistance ratio RRR ≈ 3.5 rather than the crystallinity of $CoBi_3$ itself. The low-temperature part of the curve, shown in Figure 2, displays a sharp superconducting transition at $T_c^{onset} = 0.48$ K (10 % of the transition) for zero applied magnetic field. This transition is progressively shifted towards lower temperatures for increasing magnetic field resulting in an estimate of the critical field around 2500 Oe by extrapolation of the $\mu_0 H(T_c)$ curve.

The specific heat $C_p(T)$ of the $CoBi_3$ sample, measured between 0.33 K and 2 K, is plotted in Figure 3. With decreasing temperature, $C_p(T)$ decreases monotonically and clearly exhibits a jump around $T_c = 0.45$ K, in agreement with the resistivity measurement. This observation strongly supports the bulk nature of the superconductivity. The jump is completely suppressed by an external magnetic field of 2000 Oe, again in agreement with the field dependence of $\rho(T)$. Above T_c, $C_p/T(T^2)$ decreases linearly with decreasing temperature, which allows us to fit the data between 1 K and 2 K with the Sommerfeld-Debye expression $C_p(T) = \gamma T + \beta T^3$. Here, the first and the second term correspond to the electronic and the phononic contribution to the specific heat, respectively. The resulting parameters are $\gamma = 15$ mJ mol^{-1} K^{-2} and $\beta = 3$ mJ mol^{-1} K^{-4} corresponding to a Debye

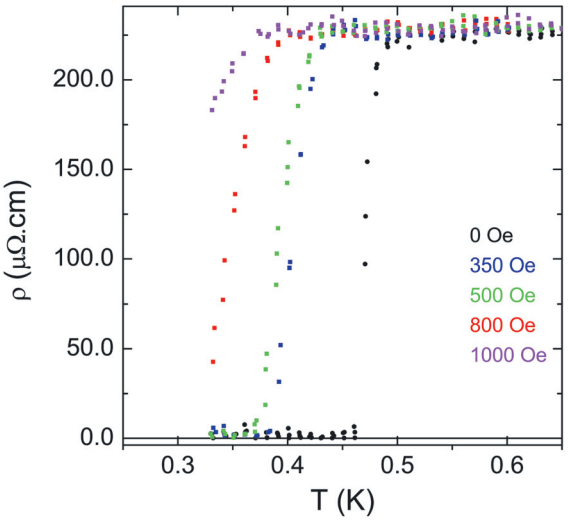

Fig. 2: Temperature dependence of the electrical resistivity of the polycrystalline $CoBi_3$ for different applied magnetic fields.

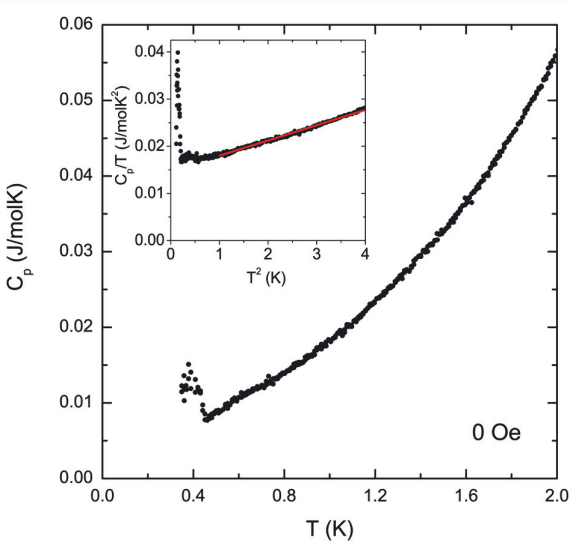

Fig. 3: Temperature dependence of the specific heat of polycrystalline $CoBi_3$. Upper inset presents the data as C_p/T vs. T^2 with the Sommerfeld-Debye fit between 1 and 2 K (solid red line).

temperature of θ_D = 137 K for the formula unit $CoBi_3$. The Sommerfeld coefficient as well as the Debye temperature are thus close to those of $NiBi_3$ (γ = 12.7 mJ mol^{-1} K^{-2}, θ_D = 144 K [3]). A quantitative analysis of the specific heat jump is hampered by the transition being close to the limit of the accessible temperature range. However, the height, $\Delta C_p/T_c$, is of the same order of magnitude as γ, a fact that indicates that the superconducting phase is likely the one associated with this γ value. Thus, the new binary phase $CoBi_3$ seems to be a low-temperature superconductor similar to its chemical analog $NiBi_3$ and $RhBi_3$.

Conclusion

We re-investigated the Co-Bi system in an effort to find new superconductors. The first binary compound, $CoBi_3$, was obtained by high-pressure, high-temperature synthesis. The metastable compound $CoBi_3$ is isostructural to $NiBi_3$ and $RhBi_3$ and decomposes at around 230 °C at ambient pressure. Preliminary investigations of the electrical resistivity and heat capacity indicate that $CoBi_3$ undergoes a superconducting transition at T_c = 0.48(3) K. Further high pressure experiments in different *TM*-Bi systems will be performed to find new and interesting superconducting compounds.

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