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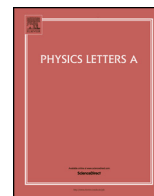
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# Superconductivity in the ternary ZrVGe compound



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## ABSTRACT

We report bulk superconductivity in ZrVGe with  $T_c = 6$  K determined by magnetization, electronic transport and specific heat measurements. From the analysis of magnetization and resistivity data we obtain the thermodynamic critical fields  $\mu_0 H_{c1}$  and  $\mu_0 H_{c2}$ , respectively. The heat capacity data deviate from conventional BCS theory suggesting possible unconventional superconducting behavior.

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## 1. Introduction

The Zr–V binary system is of interest for many applications in modern technology, in particular in steel production, electrical engineering and nuclear power systems. Surprisingly, this binary system supports a single compound ZrV<sub>2</sub> [1,2]. ZrV<sub>2</sub> is a cubic Laves phase with MgCu<sub>2</sub> structure type with superconductivity initially reported by Matthias et al. at 8.8 K [3]. However, other authors report  $T_c$  of 7.3 K for this compound [4]. But there is no data concerning the exact composition of these samples, so we can assume that  $T_c$  can vary between 7.0 and 9.0 K.

On the other hand, V–Ge alloys have been used in special applications in extreme environment conditions because of their interesting properties such as high hardness, relatively high values of melting point and extreme corrosion resistance. From the superconducting viewpoint, V<sub>3</sub>Ge found in the V–Ge binary system is with  $T_c = 6.4$  K, crystallizing in the A15 Cr<sub>3</sub>Si prototype structure [5].

Although much information about superconducting properties in binary systems like Zr–V and V–Ge has been published, we can find only a few results about the superconductivity in the ternary Zr–V–Ge system. Rudometkina et al. investigated the Zr–V–Ge ternary system and found two ternary phases of ZrVGe and Zr<sub>2</sub>V<sub>3</sub>Ge<sub>4</sub> compositions on the isothermal section at 1170 K [6].

However, they were not able to determine the crystallographic structure for these phases. Recently (1999), the crystallographic structure for the ZrVGe compound was reported [7]. This compound crystallizes in CeScSi or UGeTe prototype structure belonging to the tetragonal I4/mmm space group with lattice parameters  $a = 3.754$  Å and  $c = 14.488$  Å. This prototype structure it is similar to the quaternary LuNi<sub>2</sub>B<sub>2</sub>C which is the prototype structure of many boron-carbide superconducting materials which offer interesting opportunities for the study of multiband behavior and the coexistence between superconductivity and magnetism [8–14]. Indeed, superconductivity in layer compounds often produces unusual results and at the same time offers a modern view for the occurrence of superconductivity [9–14]. In fact, V.V. Moshchalkov et al. found superconductivity close to 4.7 K for a compound of composition around 111 [15], but the exactly composition in this case was not reported.

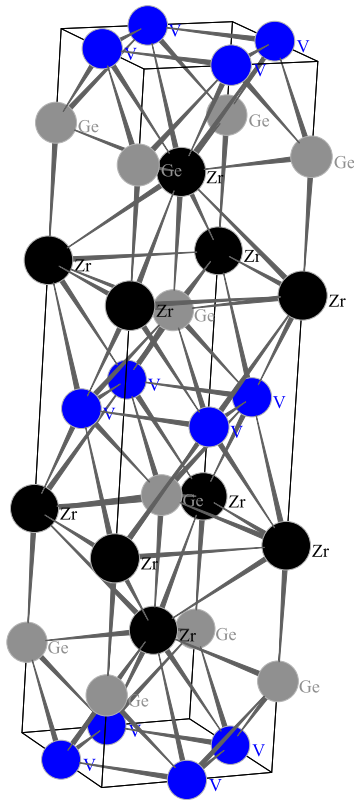
We present results that show unambiguously bulk superconductivity in the stoichiometric (111) ZrVGe compound with superconducting critical temperature close to 6.0 K.

## 2. Experimental procedure

The samples were prepared from stoichiometric mixtures of Zr, V and Ge pieces (high purity >99.999%) melted on a water cooled Cu hearth in an arc-furnace under Ar atmosphere with a Ti sponge getter. The samples were flipped over and remelted 5 times to ensure good homogeneity. Due to the low vapor pressure of these constituent elements at the melting temperatures, the weight losses during arc melting were negligible (<0.5%). A micro-

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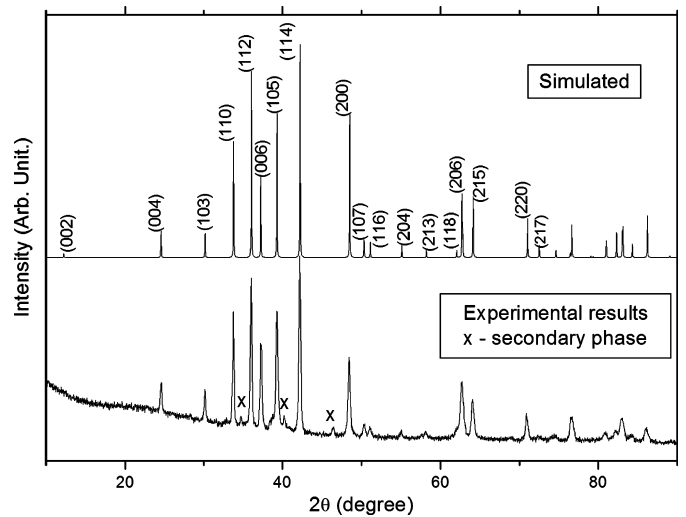
**Fig. 1.** (Color online.) Schematic structure of ZrVGe compound where the blue spheres represent vanadium atoms, gray represents germanium and black spheres represent zirconium atoms.

computer controlled diffractometer equipped with copper target for Cu  $K\alpha$  ( $\lambda = 1.54056 \text{ \AA}$ ) radiation was used to obtain powder X-ray diffraction patterns. The lattice parameters were determined using the PowderCell software and simulation [16]. Magnetic data was obtained using a commercial Quantum Design VSM-PPMS EverCool II.  $T_c$  was determined using zero field cooling (ZFC) and Field Cooling (FC), in an applied magnetic field of 2 mT. After both ZFC and FC measurements, the  $M$  versus  $H$  measurement was made at 2.0 K. Electrical resistivity measurements were made between 2.0 and 300 K using a conventional four probe method in the same device (PPMS-EverCool II). These measurements were made both without and in applied magnetic field in order to estimate the upper critical field. The specific heat of a piece cut from the sample was measured in the range of 4–10 K with a calorimeter in the PPMS (Quantum Design) using the relaxation method.

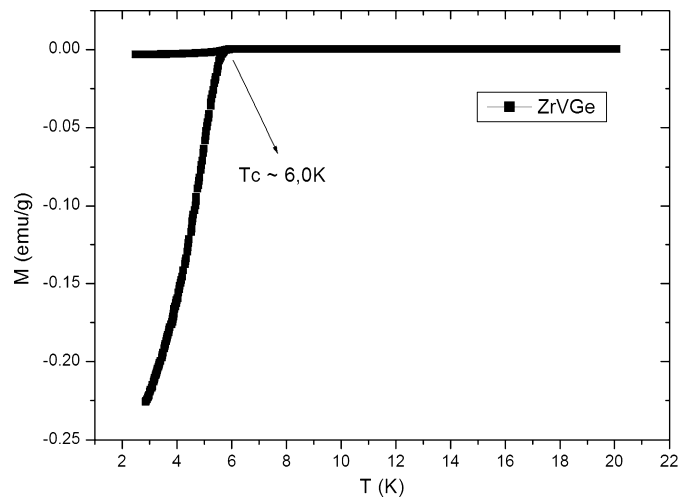
### 3. Results

**Fig. 1** shows a schematic picture of the crystalline structure simulated from PowderCell software where the blue spheres represent vanadium atoms, gray represents germanium and black spheres represent zirconium atoms. In this prototype structure the zirconium and germanium atoms occupy 4(e) site (0, 0, z) and the vanadium occupies the special position 4(c) site (0, 1/2, 0) [7].

This structure belongs to the  $I4/mmm$  space group and has lattice parameters  $a = 3.754 \text{ \AA}$  and  $c = 14.488 \text{ \AA}$ . The layer nature of this compound is clear and can be seen as a variation of the boron carbide structure whose prototype is  $\text{LuNi}_2\text{B}_2\text{C}$  [17]. Using this simulation we are able to index the X-ray patterns of the samples synthesized via arc-melting. **Fig. 2** shows the very nice agreement between simulation and experimental results. In this figure the small lines represented by an  $x$  symbol suggest minor secondary



**Fig. 2.** Comparison between simulated and experimental results showing excellent agreement.

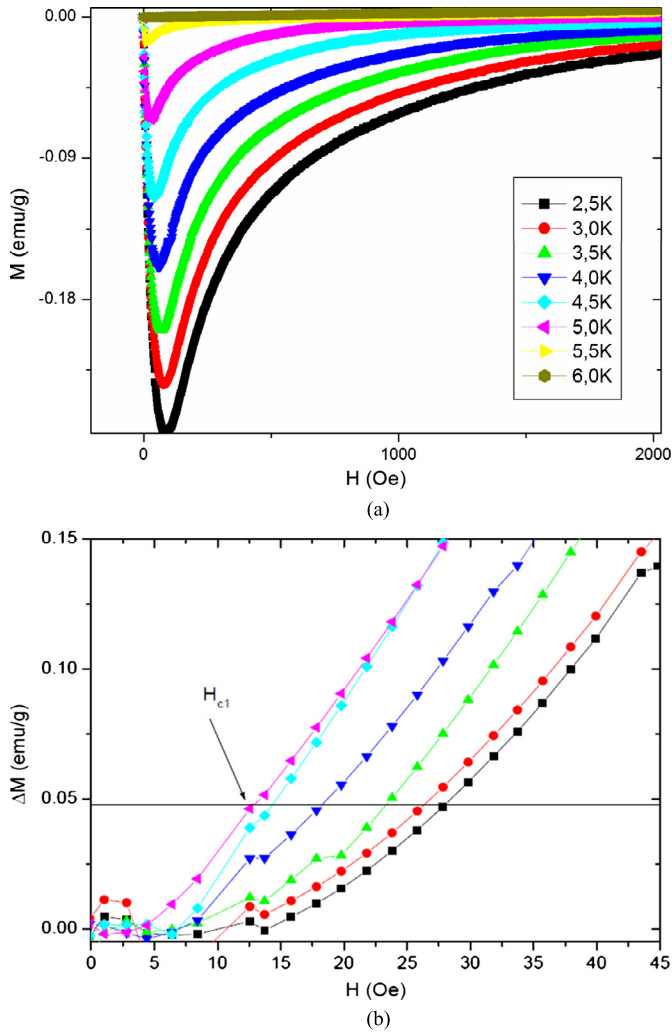


**Fig. 3.** Magnetization as a function of temperature in the ZFC and FC regimes. A clear superconducting transition appears close to 6.0 K.

phases (no identified phase). However, even in spite of this secondary phase the results suggest that the quality of the sample is very good from the crystallographic viewpoint. The position of the lines suggests that the lattice parameter used for simulation is in good agreement with experimental results. The broad shoulder observed on peak close to (105) reflection is due to the small size of the grains in our sample.

**Fig. 3** shows magnetization as a function of temperature in the zero-field cooled (ZFC) and field cooled (FC) regimes using an applied 2 mT magnetic field. This figure shows a clear diamagnetic transition at 6.0 K. The hysteresis between ZFC and FC regimes indicate ZrVGe is a type II superconductor. Without correcting for demagnetization or sample size effects, we estimate the superconducting volume fraction (ZFC) in this sample is around 97.0% of perfect diamagnetism, indicative of possible bulk superconductivity. The superconducting volume fraction can be estimated within the Meissner state through the dependence of  $M$  versus  $H$ , since the value of the superconducting state susceptibility (perfect diamagnetism) is  $-1/4\pi$ , according to the CGS system. The Meissner flux expulsion (FC) is about 5% of the diamagnetic flux expulsion (ZFC), a characteristic of strong flux pinning centers.

In order to estimate the lower critical field the  $M$  vs.  $H$  dependence was measured in the temperature interval from 2.5 to 6.0 K

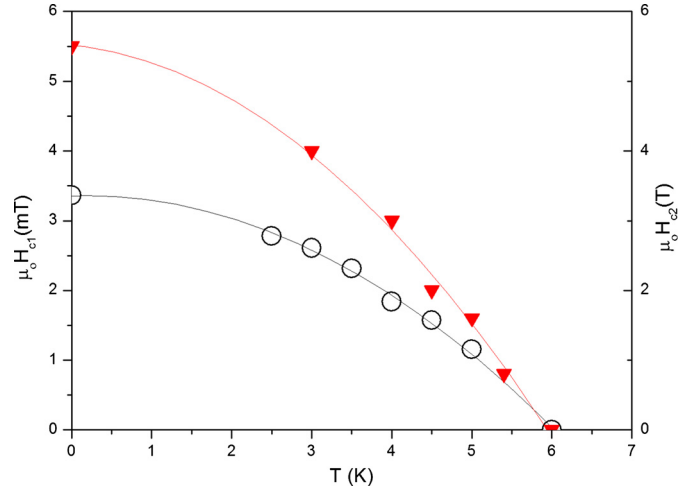


**Fig. 4.** (a) Magnetization as a function of applied magnetic field at several temperatures in the 2.5–6.0 K range. (b)  $\Delta M$  vs.  $H$  used as criterion for the lower critical field definition.

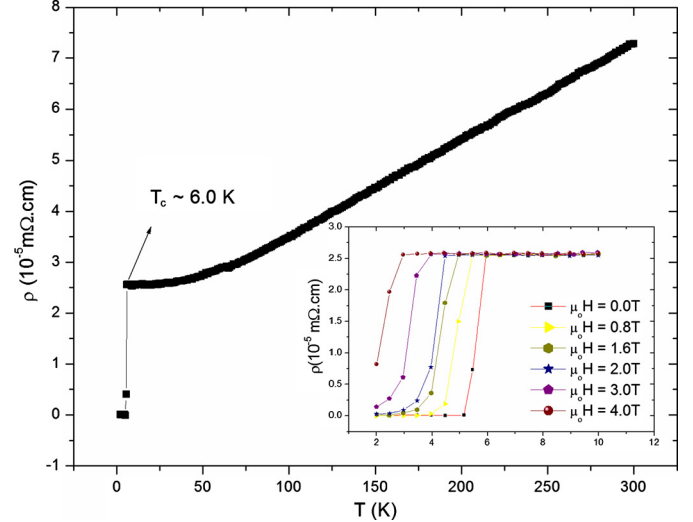
as shown in Fig. 4(a). The values of  $H_{c1}$  were determined by examining the point of departure from linearity of the slope of the magnetization curve, using  $\Delta M = 0.04762$  emu/g ( $\Delta m = 10^{-3}$  emu) as a criterion for the difference between the Meissner line and magnetization signal [18].

From the criterion used to define  $H_{c1}$  we plotted the  $\mu_0 H_{c1}$  versus temperature (see Fig. 5) and the extrapolation to zero Kelvin (see black line fitting). We found that  $\mu_0 H_{c1}$  is approximately 3.5 mT at zero temperature. Using the lower critical field from Fig. 5 at zero temperature ( $\mu_0 H_{c1} \sim 3.5$  mT), it is possible to estimate the penetration depth using the formula  $H_{c1} = \frac{\phi_0}{2\pi\lambda_L^2}$ , where the  $\lambda_L$  parameter is the penetration depth.  $\lambda_L \sim 306$  nm at zero Kelvin.

Fig. 5 also shows the upper critical field (right axis) estimated from the resistivity data shown in Fig. 6. This figure shows the resistivity as a function of temperature at zero magnetic field for a ZrVGe polycrystalline sample. The onset superconducting transition close to 6.0 K is clearly observed and the sharp transition reflects the good quality of our polycrystalline sample. This superconducting critical temperature is totally consistent with the magnetization measurement shown in Fig. 3. The inset displays the dependence of the superconducting critical temperature on applied magnetic field, showing the shift of the critical temperature typical of superconducting behavior. The magnetoresistance behavior sug-



**Fig. 5.**  $\mu_0 H_{c1}$  versus temperature showing the perfect fitting (black line) which suggests a lower critical field close to 3.5 mT at zero temperature. The red symbol means the upper critical field (right axis) where the upper critical field was estimated from WHH theory (see text). The  $\mu_0 H_{c2}$ - $T$  phase diagram was constructed using a criterion of 90% of normal state resistance, showed in Fig. 6.



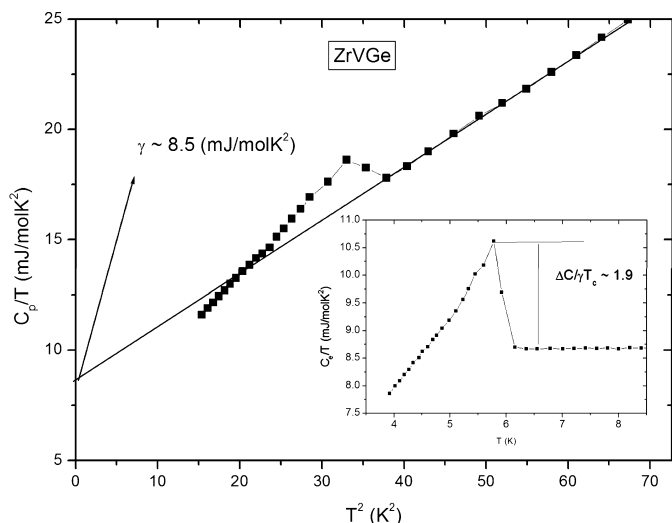
**Fig. 6.** Resistivity as a function of temperature at zero magnetic field showing the sharp superconducting transition at 6.0 K. The inset shows the magnetoresistance as a function of applied magnetic field.

gests a relatively high upper critical field ( $H_{c2}$ ) and the results are consistent with the  $M$  vs.  $T$  and  $M$  vs.  $H$  curves, and also suggest bulk superconductivity.

From the results shown in the inset of Fig. 6 we can estimate the upper critical field. The upper critical field at zero temperature ( $\mu_0 H_{c2}(0)$ ) can be estimated using the WHH formula [19] in the limit of short electronic mean-free path (dirty limit),

$$\mu_0 H_{c2}(0) = -0.693(dH_{c2}/dT)_{T=T_c} T_c.$$

In Fig. 5, the curve estimated by WHH follows the data points very closely and gives a  $\mu_0 H_{c2}(0)$  value of 5.5 T (red line). On the other hand, spin-orbit scattering counteracts the effect of the Pauli paramagnetism, giving an upper bound to  $H_{c2}$  where the pair breaking is only induced by orbital fields. The temperature dependence of the upper critical field can either be explained by Pauli paramagnetism with extremely strong spin-orbit scattering or with a dominant orbital field effect. The Pauli limiting field is described by



**Fig. 7.**  $C/T$  vs.  $T^2$  displays a jump close to 6.0 K consistent with others measurements (resistivity and magnetization). The inset shows the electronic contributions for specific heat which reveal that the  $\Delta C/\gamma T_c$  size is higher than BCS predict (1.43).

$$\mu H^{\text{Pauli}} = \frac{1.24k_B T_c}{\mu_B}$$

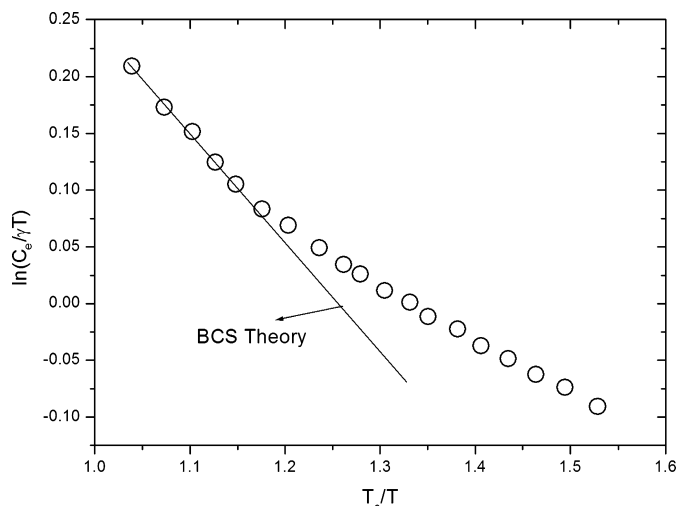
Within the same weak-coupling BCS theory this gives an upper critical field of 11.1 T, which is much higher than  $\mu_0 H_{c2}(0)$  in the absence of Pauli paramagnetism (5.5 T). Hence pair breaking in ZrVGe is most probably determined by orbital fields.

The upper critical field estimative from WHH (Fig. 5) allows an estimation of the coherence length, through use of the Ginzburg–Landau (GL) formula  $\mu_0 H_{c2}(0) = \frac{\phi_0}{2\pi \xi_0^2}$ , which yields  $\xi_0 \sim 77$  Å. The penetration depth and coherence length give the GL parameter ( $\kappa$ ) through the formula  $\kappa = \frac{\lambda_D}{\xi_0} = 39.7$  that is much larger than  $1/2^{1/2}$  is consistent with type II superconductivity.

The heat-capacity measurement is shown in Fig. 7 which displays  $C/T$  against  $T^2$  at zero magnetic field. The normal state can be fit using the expression  $C_n = \gamma + \beta T^2$  by a least-square analysis which yields  $\gamma = 8.6$  mJ/molK<sup>2</sup> ( $\sim 2.87$  mJ/K<sup>2</sup> gat; i.e. one gat is 1/3 of a mol of ZrVGe) and  $\beta = 0.24$  (mJ/molK<sup>4</sup>). This  $\beta$  value yields to Debye temperature  $\Theta_D \sim 289$  K and the value of the Sommerfeld coefficient it is proportional to the density of state at Fermi level. This result shows that ZrVGe is unambiguously a bulk superconductor. The specific heat capacity jump at  $T_c$  appears to be larger than the value for isotropic, weak coupling BCS model which can be related to strong coupling in this material [20]. The Sommerfeld constant value lies between those of MgB<sub>2</sub> ( $\sim 0.89$  mJ/K<sup>2</sup> gat) [21] and Nb<sub>3</sub>Sn ( $\sim 13$  mJ/K<sup>2</sup> gat) [22] but still relatively low in the range common for a normal metals and intermetallic compounds.

The subtraction of the phonon contribution allows us to evaluate separately the electronic contribution to the specific-heat, plotted as  $C_e/T$  vs.  $T$  in the inset of this figure (Fig. 7). An analysis of the jump yields  $\Delta C_e/\gamma_n T_c \sim 1.9$  which is somewhat higher than BCS prediction (1.43). These results could be suggesting some unconventional behavior in this material. Indeed, the specific heat  $C_s$  in the superconducting state shows marked deviations from conventional BCS theory as presented in Fig. 8. A large deviation can be observed in temperatures already close to  $T_c$ . The origin of these deviations in both figures is not so obvious but might be related to multiband behavior which is relatively common in layer compounds.

This anomaly can be associated with multiband behavior, but further measurements at lowest temperatures should be done to



**Fig. 8.**  $C_s$  of ZrVGe polycrystalline sample in the superconducting state is plotted in logarithmic scale vs.  $T/T_c$ , showing a deviation from BCS behavior.

look for a signature of a second gap. In addition, is it possible that this anomalous behavior can be also related to the impurities showed in Fig. 2. So, more experiments should be done to confirm this assumption.

#### 4. Conclusion

In this paper the superconducting properties of ZrVGe were explored. Conventional bulk superconductivity was found at  $T_c \sim 6$  K with superconducting critical fields of  $\mu_0 H_{c1(0)} = 3.5$  mT and  $\mu_0 H_{c2(0)} = 5.5$  T. The results suggest type II superconductivity with  $\kappa_{GL} = 39.7$  and bulk superconductivity was confirmed through specific heat measurements showing values of  $\gamma = 8.6$  mJ mol<sup>-1</sup> K<sup>-2</sup> and  $\beta = 0.242$  mJ mol<sup>-1</sup> K<sup>-4</sup>. The heat capacity data deviate from conventional BCS theory which could indicate some unconventional superconducting behavior in this material.

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