High pressure experimental and theoretical study of the quasi-one-dimensional sulfides AV₆S₈ (A = In, Tl)

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Abstract. We report here the results of high pressure conductivity measurements on TlₓV₆S₈ (x = 1, 0.15, 0.47, and 0.63) in pressure range from 0 - 2 GPa in the temperature range from 300 K to 300 mK to obtain insight in the competition between superconductivity and charge density waves as well as to establish the existence of a charge density wave in these materials. The experimental results are complemented by first principle electronic band structure calculations on InV₆S₈ in order to study the effect of pressure on the Fermi surface nesting which leads to the formation of the charge density wave instability.

1. Introduction

The binary vanadium-sulfur systems have generated quite some interest [1,2], because their physical properties present a border line case between compounds with localized and delocalized d-electrons. Furthermore, they are isotopic with the binary niobium chalcogenides, Nb₃X₄, which have metal zig-zag chains parallel to the crystallographic c axis. Another interesting feature of the Nb₃X₄ structure is the large hexagonal channels parallel to the c axis. They are empty in the binary niobium compounds, but occupied by In in InV₆S₈. The In atoms are statistically disordered, and the disorder is mainly one-dimensional.

The discovery of superconductivity in Tl₁V₆S₈ (x = 0.8, 0.1, and 0) by Bensch and Koy [3] has created renewed interest and have led to discovery of superconductivity in other AV₆S₈ compounds with A = In, Tl, K, Rb, and Cs by Ohtani et al. [4]. Furthermore, Ohtani et al. observed an anomaly in the temperature dependence of the resistivity in InV₆S₈ with a large hysteresis of about 40 K width, suggesting a first order phase transition. The discussed the transition in terms of a charge density wave (CDW) instability, but the lack of additional data prevented a confirmation of this suggestion.

These experimental results as well as the fact that the physical phenomena connected with the competition between structural instabilities and superconductivity are still not fully understood and motivated us to study these materials under high pressure.
There are no reports of high pressure studies of these materials, though high pressure is an excellent tool to study charge and spin density wave instabilities [5,6]. This has also been corroborated by the high pressure studies on TX₂ (T = Nb, Ta, X = S, Se) by Jerome et al. [7] and on 2H-NbSe₂ by Berthier et al. [8]. To the best of our knowledge there is only one high pressure structural study of the channel compounds, Nb₅Te₄ and InₙNb₅Te₄ (x <10) by Wunschel et al. [10].

They performed a high pressure X-ray powder diffraction study up to 40 GPa, but did not observe any phase transition. However, they found that the compression along the c axis involves the folding up of the quasi-one-dimensional zig-zag chain of Niobium. The compression perpendicular to the c axis is entirely caused by the reduction of the diameter of the channels. Furthermore, they found that the presence of intercalated In atoms have hardly any influence on the compression behavior up to 40 GPa.

Here we report now the results of high pressure conductivity measurements on TlₓV₆S₈ (x = 1, 0.15, 0.47, and 0.63) in pressure range from 0 - 2 GPa in the temperature range from 300 K to 300 mK.

Since Fermi surface nesting is necessary for a charge density wave instability [9], we have performed first principle band structure calculations which showed that Fermi surface nesting conditions are fulfilled for at least 4 different bands. Furthermore, we wanted to obtain theoretical results of the influence of pressure on the Fermi surface nesting.

2. Experimental

Samples for the high pressure conductivity measurements on TlₓV₆S₈ (x = 1, 0.15, 0.47, and 0.63) in pressure range from 0 - 2 GPa in the temperature range from 300 K to 300 mK were pressed from powder in pellets and then sintered in closed silica tubes at T = 800°C for seven days. The composition of the samples were confirmed by X-ray and microprobe analysis.

The samples were then cut in parallelepipeds and gold wires were connected on the clean surfaces with gold paste. Standard four-probe AC resistance measurements were performed at ambient and high pressure. The high pressure measurements were performed under hydrostatic conditions in a double-wall CuBe piston cylinder cell up to 2 GPa, which was designed to fit in a commercial Quantum Design PPMS. We used a mixture of n-pentane and iso-pentane as pressure medium, which ensured excellent hydrostatic conditions. The shift of the superconducting transition temperature, Tₛ, of a Pb sample used as manometer, was determined using a four-probe AC resistance measurement and then converted into pressure using the Tc(p) calibration from Eiling et al. [11]. No pressure gradient was observed when a larger Pb sample was covering the whole sample space. Its superconducting transition width remained narrow (ΔTc ≈ 5 mK) and almost pressure independent.

3. Crystal structure

The crystal structure of InV₆S₈ is based on a hexagonal cell [4] of Nb₅Te₄-type (space group P6₃) [12] with room temperature ambient pressure values of a = 9.207 Å and c = 3.310 Å. The structure is composed of V₆S₈ octahedra linked together by shared edges and faces to form hexagonal channels running parallel to the crystallographic c axis [13].

Another notable feature of the structure is the existence of V-V zig-zag chains. They run along the c-axis and are well isolated from each other with an intrachain distance of 2.864 Å and an interchain distance of 3.150 Å.

4. Details of theoretical calculations

For a better understanding of the high pressure effects in this quasi-one-dimensional system, we have carried out the electronic band structure calculations for InV₆S₈, both at ambient and at 18 GPa pressure. We employed the full potential linear augmented plane wave (FPLAPW) method as implemented in the WIEN2K code [14]. As there is random occupation of the two equivalent In-sites in the unit cell, each with probability of 0.5, we have adopted the virtual crystal approximation [15] in our band structure calculations. As unit cell we have taken a simple hexagonal cell. The valence
electronic configuration of In, V, and S are taken as, [Ar]3d\(^{10}\)4s\(^2\), and [Ne]3s\(^2\)3p\(^4\), respectively. As the 4d states of In are well below the Fermi level (by about 10 eV), and mainly its wide-band 5s\(^2\) states contribute to the conduction band, our virtual crystal approximation for disorder at In sites should be adequate. For the exchange-correlation terms, we have used the local density approximation as per Perdew-Wang [16] re-parameterization of Ceperley-Alder data [17].

In\(_3\)V\(_6\)S\(_8\) crystallizes in a primitive hexagonal lattice with 16 atoms per unit cell, and our ADXRD measured lattice constants have been used in the calculations. The fractional coordinates of atomic positions in the unit cell have been taken as per Ref.13 at all compressions, though ideally a study of the variations of these coordinates under compression is desired. As it is well-known, the basis functions in the FPLAPW method depend upon the plane waves used in the interstitial region. Therefore, we have employed about 3100 plane waves (\(R_mK_{\max} = 7\) in WIEN2K, where \(R_m\) is the muffin-tin radius and \(K_{\max}\) determines the wave-vector cut-off for the plane wave expansion). \(R_m\) has been fixed at 1.4 atomic units (a.u.-Bohr radius) for In, 1.5 a.u. for V and 1.5 a.u. for S. We have used 500 \(k\)-points for Brillouin zone (BZ) sampling (70 \(k\)-points in the irreducible wedge of the BZ).

5. Results and discussion

5.1. Experimental

Fig. 1 shows the pressure dependence of the CDW instability in \(T_{10.63}V_6S_8\), because this material displays both, a CDW instability and full superconductivity. Upon applying hydrostatic pressure the CDW anomaly size is gradually reduced together with a decrease of \(T_l\) and \(T_h\), the temperatures where \(\delta \rho/\delta T\) as a function of \(T\) has a local minimum upon cooling and warming up, respectively.

![Figure 1. Pressure dependence of the CDW instability upon warming up.](image)

The behavior of the hysteresis in the resistivity is maintained up to \(p = 1.26\) GPa. Above this pressure, which corresponds to \(T_l = 95\) K, any signature of the anomaly upon cooling down is difficult to be unambiguously resolved. However, the anomaly is still visible when the sample is warmed up. And can be followed up to \(p = 1.71\) GPa corresponding to \(T_h = 67\) K. For even higher pressure, the transition at \(T_h\) is suddenly suppressed. We estimate a critical pressure for the suppression of the CDW instability to be about \(p_c = (1.85 \pm 0.12\) ) GPa. The combined results of the pressure dependence of \(T_h\) and \(T_l\), as well as the superconducting transition temperature, \(T_c\), are displayed in Fig. 2.
5.2. Theoretical

Our calculated band structures are shown in Figs. 3 and 4. The energy range is reduced in Figs. 3 and 4, so that only bands near the Fermi level are shown. The one-dimensional nature of the system is revealed in Fig. 3, since the bands are more dispersive along \( \Gamma A \) direction compared to those in planes normal to \( \Gamma A \) and the half-filled bands exist only along \( \Gamma A \). At higher compression (Fig. 4) bands in the planes normal to \( \Gamma A \) also cut the Fermi level indicating that compression tends to destroy the quasi-one-dimensional nature of In\( \text{V}_6\)S\( \text{8} \), though the relative dispersion of the bands are not drastically changed. The most interesting effect is that the degenerate energy level at \( A \) which is below \( E_F \) at \( V/V_0 = 1 \) is shifted up in energy and is located above \( E_F \) at \( V/V_0 = 0.88 \) (Fig. 4).

This shift corresponds to the main dissimilarity seen in the corresponding Fermi surface sheets, shown in Figs. 5 and 6 in the \( \Gamma^7-A-H-K \) plane of the BZ.

Figure 2. The phase diagram of Tl\( \text{0.63V}_6\)S\( \text{8} \). The CDW instability is completely suppressed at a critical pressure \( p_c = (1.85 \pm 0.12) \) GPa and concomitantly \( T_c \) is enhanced (inset). The dashed lines are guides for the eye.

Figure 3. Energy bands of In\( \text{V}_6\)S\( \text{8} \) at ambient pressure \( (V/V_0 = 1) \).

Figure 4. Energy bands of In\( \text{V}_6\)S\( \text{8} \) at a compression of \( V/V_0 = 0.88 \).
We first discuss the Fermi surface sheets shown in Fig. 5, which corresponds to the band structure depicted in Fig. 3 (ambient pressure). As we can see from Fig. 3, the Fermi level intersects 6 electron bands as the k-vector increases along the \( \Gamma - A \) direction from zero to \( \Gamma A \). Their positions are labeled by 1 – 6 in Fig. 5 along the \( \Gamma - A \) direction. These can be considered as 3 electron sheets (1 – 3) centered around \( \Gamma \) (with \( K - \Gamma - K \) as axis), an electron sheet (6) around \( A \) (with \( H - A - H \) as axis) and a sheet which can be considered as a hole sheet around a point at a distance of 0.7 \( \Gamma A \) from \( \Gamma \) along \( \Gamma - A \) (shown as open circles to identify it separately) formed by bands 4 and 5, as these two bands intersect each other a little above the Fermi level (see Fig. 3). The sheet arising from the band labeled 1 has a considerable region with parallel parts, connected by some k-vector (nesting) parallel to the \( \Gamma - A \) direction. As can be seen from Fig. 6, this part of the nesting is retained almost to the same extent at a higher compression of \( V/V_0 = 0.88 \). There are also less prominent nesting regions of the band 3 sheet, again with nesting k-vectors in the \( \Gamma - A \) direction, near the \( K \)-point and to a lesser extent near the \( \Gamma \)-point. The bands 2 and 4 also show some nesting near the \( \Gamma \)-point. The nesting is, however, negligible for bands 5 and 6. There are also inter-band nesting regions between bands 2, 3, and 4 as the sheets of these bands are parallel where they intersect the \( \Gamma - A \) line. All these nesting properties are more or less retained at the compressed volume, as can be seen in Fig. 6. Thus the main difference is the merging
of sheets corresponding to the bands 5 and 6, which arises due to the shift of the energy level near the A-point, discussed earlier, thus making the sheet around the A-point for band 6 more hole-like. Therefore, we can conclude, that for this quasi-one-dimensional system, the nesting properties of the Fermi surface sheets are not drastically affected by compression, at least up to \( V/V_0 = 0.88 \), which corresponds to about 18 GPa. Whether the loss of the quasi-one-dimensionality, seen already in Fig. 4 affects the electron-phonon interaction, and thus the charge density wave instability, is a different aspect and needs studies beyond the band structure calculations.

6. Summary
We have measured the pressure dependence of \( T_s \) and \( T_I \) of the CDW instability as well as the pressure dependence of the superconducting transition temperature, \( T_c \), and determined the phase diagram for \( \text{Th}_{0.63}\text{V}_6\text{S}_8 \). The observed hysteresis upon cooling and warming shows that the transition at \( T_s \) is a first order phase transition. Band structure calculations of InV\(_6\)S\(_8\) up to a compression of \( V/V_0 = 0.88 \) do not show a significant change in the main nesting contours of the Fermi surface sheets, but reveal a topological transition along the \( \tau A \) direction. The quasi-one-dimensionality is lost, or at least considerably reduced at this compression.

There are open questions connected with the quality of the samples. High quality single crystals are now available for these studies, in particular high pressure X-ray diffraction measurements at low temperatures will be crucial to understand the underlying physics. In addition, improvements of the band structure calculations by going beyond the Virtual Crystal Approximation (VCA) would be desirable to see, if our assumption that the VCA adequately takes into account the In disorder.

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