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# First-order phase transition in the ternary sulfide $\text{NiV}_2\text{S}_4$

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## Abstract

We report our investigations of the electrical resistivity, Seebeck coefficient, thermal conductivity, and heat capacity on the ternary sulfide  $\text{NiV}_2\text{S}_4$  as a function of temperature. All measured physical quantities exhibit pronounced anomalies at around 165 K, with a significant hysteresis of about 10 K. The results of electrical transport measurements show conventional metallic-like characteristics below and above the transition, indicative of the first-order metal–metal transition in  $\text{NiV}_2\text{S}_4$ . The anomalous features of  $\text{NiV}_2\text{S}_4$  are compared to those of other thiospinels, and possible origins responsible for the present transition are provided.

## 1. Introduction

Transition metal-based spinel-type sulfides are of considerable interest due to their unusual transport and magnetic properties. Superconductors (e.g. in  $\text{CuRh}_2\text{S}_4$ ), [1] magnetic insulators (e.g. in  $\text{CuIr}_2\text{S}_4$ ), [2, 3] and charge density waves (CDWs) (e.g. in  $\text{CuV}_2\text{S}_4$ ) [4, 5] have been found to exist in this class of materials. The variety of physical behaviour observed in these sulfides seems to be strongly associated with different types of phase transition. For example,  $\text{CuIr}_2\text{S}_4$  undergoes a metal–insulator (M–I) transition at around 230 K simultaneously with a structural transition from the cubic to tetragonal phase [2, 3]. Detailed structural studies have revealed that the phase transition is accompanied by charge ordering and spin dimerization [6]. It has been argued that the occurrence of spin dimerization in such a three-dimensional compound is a unique event, and the true mechanism for the phase transition of  $\text{CuIr}_2\text{S}_4$  still remains an open question.

In addition to the cubic thiospinels, a great number of ternary sulfides with the general formula  $AB_2S_4$  crystallize in the  $\text{Cr}_3\text{S}_4$  structure as two nonequivalent Cr crystallographic sites (Wyckoff positions 2a and 4i with population ratio 1:2) are occupied by different elements [7–10]. Although materials of this prototype exhibit a wide variety of interesting physical properties, relatively few studies on these systems have been reported as compared to

the spinel-type sulfides.  $\text{NiV}_2\text{S}_4$ , which is isostructural to  $\text{Cr}_3\text{S}_4$ , has been noticed to show a drop in the magnetic susceptibility at around 180 K [11, 12]. The feature has been ascribed to the possible occurrence of a magnetic ordering or crystallographic transition. Alternatively, the formation of CDWs like the spinel  $\text{CuV}_2\text{S}_4$  could lead to a similar signature in the vicinity of the transition [4, 5]. However, no corresponding anomalies have been observed in the previously reported resistivity and Seebeck coefficient data [11, 13].

In order to examine the existence and/or nature of the phase transition in  $\text{NiV}_2\text{S}_4$ , we have carried out a detailed study by measuring the electrical resistivity ( $\rho$ ), Seebeck coefficient ( $S$ ), thermal conductivity ( $\kappa$ ), and heat capacity ( $C_p$ ) on the titled material, especially near the transition temperature. Our results clearly show substantial variations across the phase transition with significant thermal hysteresis in all measured physical properties, demonstrating the first-order character of the phase transition. Possible origins for the observed phase transition in  $\text{NiV}_2\text{S}_4$  are also given.

## 2. Experiment and discussion

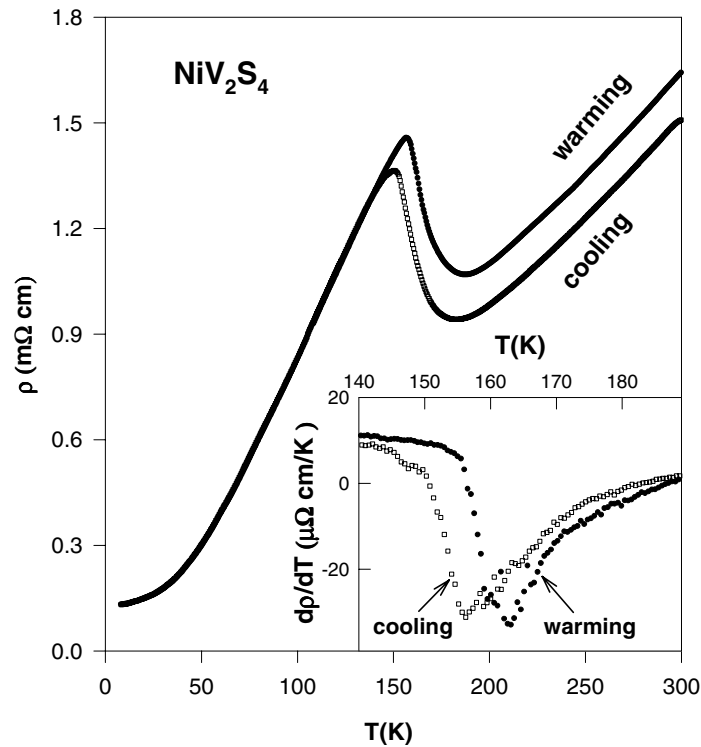
Polycrystalline  $\text{NiV}_2\text{S}_4$  was prepared by a conventional solid-state reaction method. A mixture of high-purity powders of Ni, V, and S with nominal stoichiometry was sealed in an evacuated quartz tube and calcined at 800 °C for seven days. A room-temperature x-ray diffraction pattern of the powder sample taken with Cu  $K\alpha$  radiation indicates the expected structure, with several weak peaks which could be indexed to the diffraction planes of  $\text{V}_2\text{O}_3$ . The presence of  $\text{V}_2\text{O}_3$  is not trivial because this material undergoes an antiferromagnetic (metal–insulator) transition at around 150 K, very close to the transition temperature of  $\text{NiV}_2\text{S}_4$  [12]. However, we will demonstrate later that the observed phase transition here is an intrinsic characteristic of  $\text{NiV}_2\text{S}_4$  rather than an extrinsic effect arising from  $\text{V}_2\text{O}_3$ .

Electrical resistivity measurements were carried out using the standard four-probe method. Seebeck coefficient and thermal conductivity experiments were simultaneously performed using the direct heat pulse technique. The relative heat capacity was obtained from a high-resolution ac calorimeter, using chopped light as a heat source. More details of the measurement techniques can be found elsewhere [14, 15].

The temperature-dependent electrical resistivity  $\rho(T)$  of  $\text{NiV}_2\text{S}_4$  is displayed in figure 1. Upon lowering the temperature,  $\rho$  decreases rather linearly and then exhibits a sharp upturn between 155 and 175 K. With further cooling,  $\rho$  decreases again, indicating conventional metallic behaviour below and above the transition temperature. In this regard, the present feature could be characterized as a metal–metal (M–M) transition, and the pronounced thermal hysteresis establishes the first-order character of the transition. The transition temperatures are 155 and 165 K, determined from the position of the negative dip in  $d\rho/dT$  for cooling and warming runs respectively, as illustrated in the inset of figure 1.

Other interesting features of  $\rho$  are that the heating curve lies above the cooling curve and that these curves do not merge at high temperatures. However, as one will see later, no such a phenomenon appears in the heat capacity measurement. The earlier studied system of  $\text{Lu}_2\text{Ir}_3\text{Si}_5$ , which also exhibits similar behaviour [16], suggests that residual stresses presumably induced by a structural transformation may significantly affect the electrical transport properties, but have little or no effect on the thermodynamic characteristics. We believe that such an argument is also appropriate to the present case of  $\text{NiV}_2\text{S}_4$ .

Figure 2 shows the temperature-dependent Seebeck coefficient  $S(T)$  for  $\text{NiV}_2\text{S}_4$ . The room-temperature value of  $S$  is about  $-2.5 \mu\text{V K}^{-1}$ , which is consistent with the earlier reports [12, 13]. The values of Seebeck coefficient are negative in the temperature range we investigated, signifying that  $\text{NiV}_2\text{S}_4$  is an n-type material. The phase transition of  $\text{NiV}_2\text{S}_4$

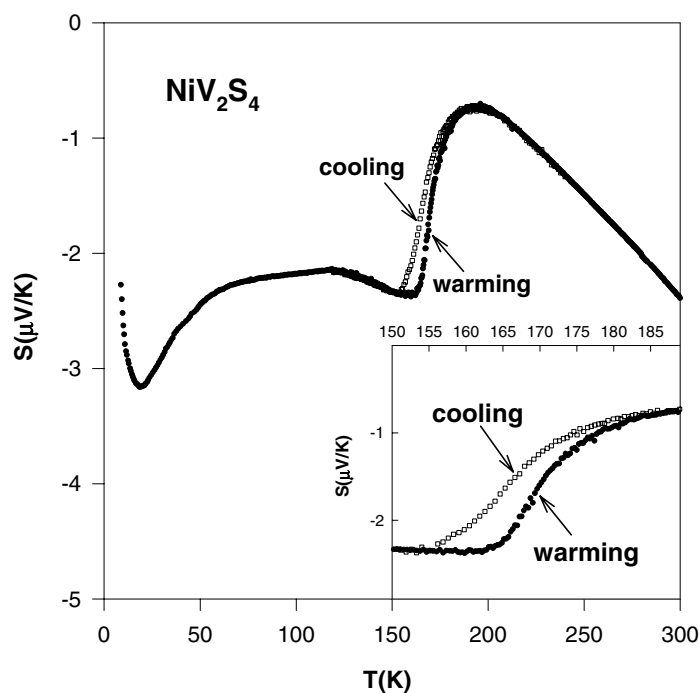


**Figure 1.** Temperature dependence of the electrical resistivity for  $\text{NiV}_2\text{S}_4$ . Inset: a  $d\rho/dT$  versus  $T$  plot with regards to the transition temperatures.

manifests itself by the abrupt change in  $S$ . The hysteresis loop of about 10 K (see the inset of figure 2) is a further proof of the first-order nature for the transition. Below the transition temperature,  $S$  exhibits a weak temperature variation followed by a minimum at about 20 K which is a typical consequence of the phonon drag effect. The observations of the linear diffusive behaviour above the transition and the presence of the low-temperature phonon drag are in accordance with conventional metallic characteristics. The nonlinear variation below the transition is presumably masked by the onset of the phonon drag effect.

The temperature-dependent thermal conductivity  $\kappa(T)$  of  $\text{NiV}_2\text{S}_4$  is given in figure 3. With lowering temperature, a monotonic decrease in  $\kappa$  is followed by a step-like jump across the phase transition at around 165 K. Below the phase transition,  $\kappa$  continuously increases up to  $\sim 50$  K, developing into a broad maximum, and then drops rapidly at low temperatures. This is a typical feature for the reduction of thermal scattering at low temperatures for solids. A small but still noticeable hysteresis occurs between the cooling and warming data. The details of  $\kappa$  within the transition region are shown in the inset of figure 3.

Since the results of thermal conductivity measurements provide valuable information about various scattering processes of thermal carriers, the present data would offer an opportunity to probe the interplay between the lattice and charge degrees of freedom in this compound. In general, the total thermal conductivity for a metal can be expressed as a sum of lattice ( $\kappa_L$ ) and electronic ( $\kappa_e$ ) terms:  $\kappa = \kappa_L + \kappa_e$ . The electronic contribution is estimated by means of the Wiedemann–Franz law:  $\kappa_e \rho / T = L_0$ . Here  $\rho$  is the dc electrical resistivity and  $L_0 = 2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$  is the Lorentz number. We thus calculated  $\kappa_e$  (dashed line) using



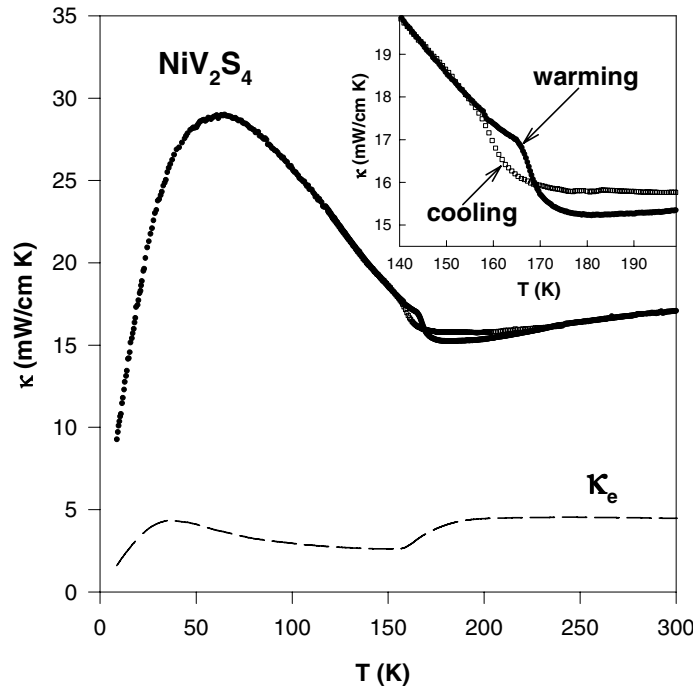
**Figure 2.** Seebeck coefficient versus temperature for  $\text{NiV}_2\text{S}_4$ . The inset represents the thermal hysteresis behaviour in the vicinity of the transition.

the Wiedemann–Franz law and measured  $\rho$  data. It is apparent that the abrupt upturn in the vicinity of the transition is not due to the electronic contribution, but is essentially caused by the increase of lattice thermal conductivity [17]. Such a result suggests that the strong electron–phonon coupling, which could arise from phonon softening, results in a Kohn anomaly near the phase transition [18].

Heat capacity measurement is known as a sensitive probe of phase transitions involving entropy change. The measured heat capacity data of  $\text{NiV}_2\text{S}_4$  reveal two distinct features at around 165 and 190 K, as shown in figure 4. The former, corresponding to the M–M transition observed in the transport measurements, is first order, with a hysteresis loop of about 4 K (see the inset of figure 4). Here the weak variation in  $C_P$  indicates that the entropy involved with the M–M transition is rather small.

Another peculiar feature in  $C_P$  is the appearance of a second jump near 190 K, which lacks thermal hysteresis. Since there are no corresponding anomalies in the transport results, the antisite disorder between Ni and V atoms in the nominal phase of  $\text{NiV}_2\text{S}_4$  may be the possible mechanism for the 190 K phase transition. As mentioned by Powell *et al* [8], the appearance of an inversion structure of  $\text{V}[\text{NiV}]\text{S}_4$  has been detected in a real sample. We thus speculate that the phase of  $\text{V}[\text{NiV}]\text{S}_4$  may have an undetermined second-order transition near 190 K. Even though only a small amount of  $\text{V}[\text{NiV}]\text{S}_4$  exists in the specimen, it is still visible in the heat capacity data because  $C_P$  is very sensitive to the existence of phase transitions.

$^{63}\text{Cu}$  NMR Knight shift measurements in  $\text{CuIr}_2\text{S}_4$  exhibited a discontinuous change below the transition temperature [19], attributed to the loss of the contribution from conduction electrons, being consistent with the insulating phase at low temperatures (metal–insulator transition). On the other hand, our preliminary  $^{51}\text{V}$  NMR Knight shift data showed a marginal

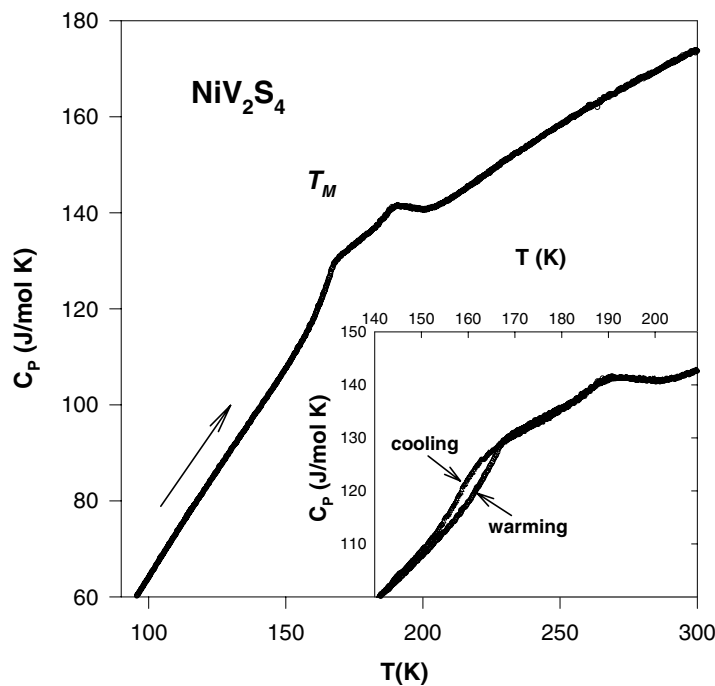


**Figure 3.** Thermal conductivity as a function of temperature for  $\text{NiV}_2\text{S}_4$ . The estimated electronic contribution ( $\kappa_e$ ) to the total thermal conductivity is drawn as a dashed line. Inset: a close-up plot for the observed thermal hysteresis in  $\kappa$  near the phase transition.

variation below the transition temperature of  $\text{NiV}_2\text{S}_4$  [20]. This observation is in good agreement with the response of the metal–metal transition in  $\text{NiV}_2\text{S}_4$ . Moreover, we found no marked broadening in the  $^{51}\text{V}$  resonance spectrum at low temperatures, indicating that the transition is not driven by the magnetic ordering. Such a finding also reinforces the conclusion that the impurity phase of  $\text{V}_2\text{O}_3$  has little effect on the phase transition we address here because  $\text{V}_2\text{O}_3$  is a type of antiferromagnetic material at low temperatures.

The present investigation shows clear evidence of a first-order phase transition at around 165 K in  $\text{NiV}_2\text{S}_4$  involved with substantial changes in the electronic structure. In fact, the observed phase transition in  $\text{NiV}_2\text{S}_4$  is very likely due to the periodic displacement of the crystal lattice/lattice distortion, as implied by the present transport measurements and previously made predictions [12]. In addition, the dramatic changes in the thermoelectric property suggest that the electronic structure of  $\text{NiV}_2\text{S}_4$  is significantly modified as the lattice distortion occurs. The formation of CDW coupled with such crystallographic changes may give rise to appreciable changes in the electronic density of states (DOS). In particular, the variations become well pronounced when the Fermi level is located at a position with rapidly varying DOS. Indeed, the anomalous features presented here are reminiscent of those in the low-temperature incommensurate–commensurate CDW transition for  $\text{CuV}_2\text{S}_4$  [21, 22]. However, the conclusive evidence for a CDW transition in  $\text{NiV}_2\text{S}_4$  will have to wait until there has been an exact phase identification of the superlattice by high-resolution x-ray diffraction.

One may speculate that the band Jahn–Teller effect is responsible for the origin of this phase transition [23], simply from the consideration of ionic configurations for  $\text{NiV}_2\text{S}_4$ . Taking the well-defined oxidation states of  $\text{Ni}^{2+}$  and  $\text{S}^{2-}$ , the reasonable ionic configurations would



**Figure 4.** Temperature-dependent specific heat of  $\text{NiV}_2\text{S}_4$  measured on warming. The inset shows the thermal hysteresis near the 165 K first-order transition and the 190 K second-order transition.

be either  $\text{Ni}^{2+}\text{V}_2^{3+}\text{S}_4^{2-}$  or  $\text{Ni}^{2+}\text{V}^{2+}\text{V}^{4+}\text{S}_4^{2-}$ . Since the ionic radii for  $\text{V}^{2+}$ ,  $\text{V}^{3+}$ , and  $\text{V}^{4+}$  are different, crystal distortion associated with these two arrangements during the transition seems possible. However, the structure already contains one-dimensional character and thus  $\text{V}^{4+}$  ion is not particularly favoured in such a sulfide matrix. Therefore, the association between the present phase transition and the band Jahn–Teller mechanism is not quite possible for the case of  $\text{NiV}_2\text{S}_4$ .

In summary, a first-order metal–metal transition in  $\text{NiV}_2\text{S}_4$  has been revealed through the present transport and thermal measurements. From the observed features in the vicinity of the transition temperature, the transition is very likely due to the periodic displacement of the crystal lattice associated with electronic origins, and CDW formation may be the origin for the presently observed anomalies.

### Acknowledgments

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