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Electronic and magnetic properties of V_5S_8

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Abstract. The electronic properties of monoclinic V_5S_8 in its paramagnetic, ferromagnetic and antiferromagnetic states have been studied by means of the linear muffin-tin orbital method of band-structure calculation. On the basis of the corresponding results, the magnetic properties of V_5S_8 are discussed in comparison with experimental data stemming from neutron scattering and nuclear magnetic resonance.

1. Introduction

Transition-metal chalcogenides show a great variety in their various physical properties. This applies in particular as regards magnetism. For example, VS and V_3S_4 show weak temperature-independent paramagnetism, whereas V_5S_8 shows a Curie–Weiss behaviour at high temperature. At low temperature, on the other hand, V_3S_4 and V_5S_8 order antiferromagnetically with Néel temperatures of $T_N = 8$ and 32 K, respectively.

V_5S_8 , which will be investigated here, shows metallic conductivity for all temperatures. Its monoclinic structure [1, 2] can be described as a superstructure of an ordered arrangement of vanadium vacancies in a NiAs-type fundamental structure. Nuclear magnetic resonance (NMR) studies have shown that only V atoms (type 1) in the vacant layers have magnetic moments [3–5]. From their NMR experiments, Kitaoka *et al* [6] have deduced a magnetic moment of $0.22 \mu_B$ for the V1 site. On the other hand, the effective paramagnetic moment μ_{eff} derived from magnetic susceptibility data [3, 5, 7] lies between 2.12 and $2.49 \mu_B$. Magneto-torque measurements on single crystals were carried out by various groups [8, 7] to investigate the anisotropy of the magnetic properties of V_5S_8 . In addition, the magnetic structure has been investigated by means of neutron diffraction at low temperature by Funahashi, Nozaki and Kawada [9] for two single crystals. The magnetic moments deduced for these two samples— 0.7 and $1.5 \mu_B$, respectively—are much larger than those stemming from NMR measurements.

Because of the complex crystal structure of V_5S_8 , no theoretical investigation of its electronic and magnetic structure has been made so far. In the following, results of corresponding *ab initio*, self-consistent spin-polarized band-structure calculations are presented. These are compared with the observed physical properties and are used in particular to discuss the magnetic properties of V_5S_8 .

2. Details of the band-structure calculation

For the band-structure calculation, the tight-binding linear muffin-tin orbital (TB-LMTO) method of Andersen and Jepsen [10] was used. Relativistic effects have been accounted for by using the scalar-relativistic approximation ignoring the influence of spin-orbit coupling. For the calculation, the atomic sphere approximation (ASA) was used, together with the so-called combined correction terms. To fill the open regions of the crystal structure, two types of empty sphere were introduced. For the V atoms the 3d, 4s and 4p functions were used as the basis, while for the S atoms the basis consisted of 3s, 3p and 3d functions. Exchange and correlation have been treated within the framework of the local density functional theory [11, 12] using the parametrization of von Barth and Hedin [13]. All of the results presented here have been obtained by using the tetrahedron method, performing the necessary Brillouin zone (BZ) integration. For the paramagnetic case, 554 k -points, and for the antiferromagnetic case, 70 k -points were used during the SCF cycle.

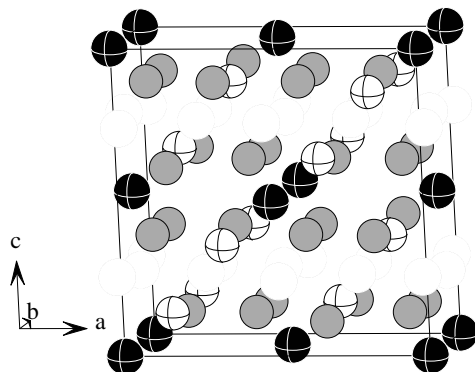


Figure 1. The monoclinic unit cell of V_5S_8 for the paramagnetic state. Key: V1: black, with cross; V2: black, with vertical hatching; V3: black, with horizontal hatching; S1: white, with cross; S2: white, with vertical hatching; S3: white, with horizontal hatching.

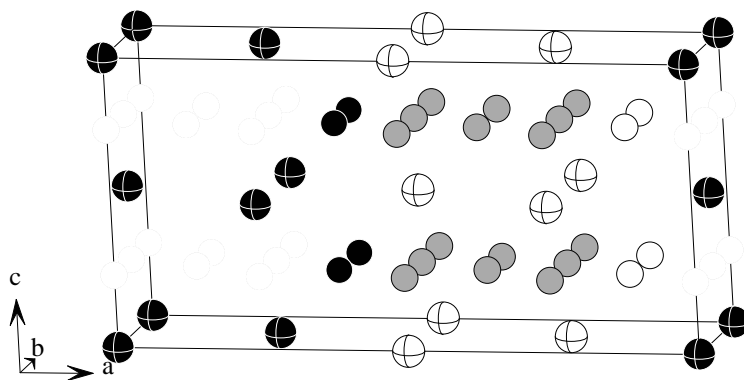
3. Spatial and magnetic ordering of V_5S_8

V_5S_8 crystallizes in a monoclinic structure having the space group $C2/m$ (space group number 12). The corresponding unit cell is shown in figure 1. As already mentioned, the structure is closely related to the NiAs structure that is adopted by VS at high temperature and in the case of non-stoichiometry, i.e. for a V deficit. For the perfectly ordered V_5S_8 , in every second metal layer perpendicular to the c -axis, three-quarters of the V atoms are missing compared to the NiAs structure. The V atoms in this layer are denoted as type 1 positioned at sites a. For the full metal layers, the VS_6 octahedra share common edges. The V atoms on these layers consist of V atoms of type 2 and 3 positioned at the sites g and i, respectively. Octahedra in fully occupied layers are connected to octahedra centred on the partially depleted layers via common faces. In these partially depleted layers the V atoms have the same local symmetry as V atoms in VS_2 crystallizing in the CdI_2 structure.

The lattice parameters have been taken from experiment [2] and are tabulated in table 1. The distance between V1 and V3 is 2.92 Å and is therefore comparable to the V–V distance in pure vanadium metal. The distance between V2 and V3 (3.00 Å) is much bigger and is comparable with the V–V distance occurring for VS having the NiAs structure.

Table 1. Parameters for the crystallographic unit cell and Wigner–Seitz sphere radii used in the band-structure calculation of V_5S_8 . In addition the corresponding V–S distances are given.

Lattice constants	a	11.356 Å
	b	6.648 Å
	c	11.298 Å
	β	90.60°
V1–V3 distance		2.920 Å
V2–V2 distance		2.826 Å
V2–V3 distance		3.001 Å
(V1–S) distance		2.400 Å
(V2–S) distance		2.386 Å
(V3–S) distance		2.391 Å
Wigner–Seitz radii	r_{V1}	1.559 Å
	r_{V2}	1.488 Å
	r_{V3}	1.488 Å
	r_{S1}	1.497 Å
	r_{S2}	1.439 Å
	r_{S3}	1.477 Å
	r_{E1}	1.417 Å
	r_{E2}	1.388 Å

**Figure 2.** The monoclinic unit cell of V_5S_8 for the antiferromagnetic state. The S atoms have been omitted for the sake of clarity. Key: V1 \uparrow : black, with cross; V2 \uparrow : black, with vertical hatching; V2 $_0\uparrow$: solid black; V3 $_A\uparrow$: black, with horizontal hatching; V3 $_B\uparrow$: black, with diagonal hatching; V1 \downarrow : white, with cross; V2 \downarrow : white, with vertical hatching; V2 $_0\downarrow$: solid white; V3 $_A\downarrow$: white, with horizontal hatching; V3 $_B\downarrow$: white, with diagonal hatching.

The antiferromagnetic unit cell, as deduced from neutron scattering measurements [9], is shown in figure 2. As one notes, the magnetic structure causes a doubling of the unit cell along the a -axis with respect to the crystallographic cell. Because the antiferromagnetic unit cell has a primitive monoclinic Bravais lattice instead of a base-centred monoclinic crystallographic Bravais lattice, the antiferromagnetic unit cell contains four times more atoms than the crystallographic one. Due to magnetic ordering, the atoms are further divided into two subtypes for all above-mentioned atom types except V1 atoms. For symmetry reasons, the V2 $_0$ atoms are non-magnetic. All other atoms could in principle carry a magnetic moment.

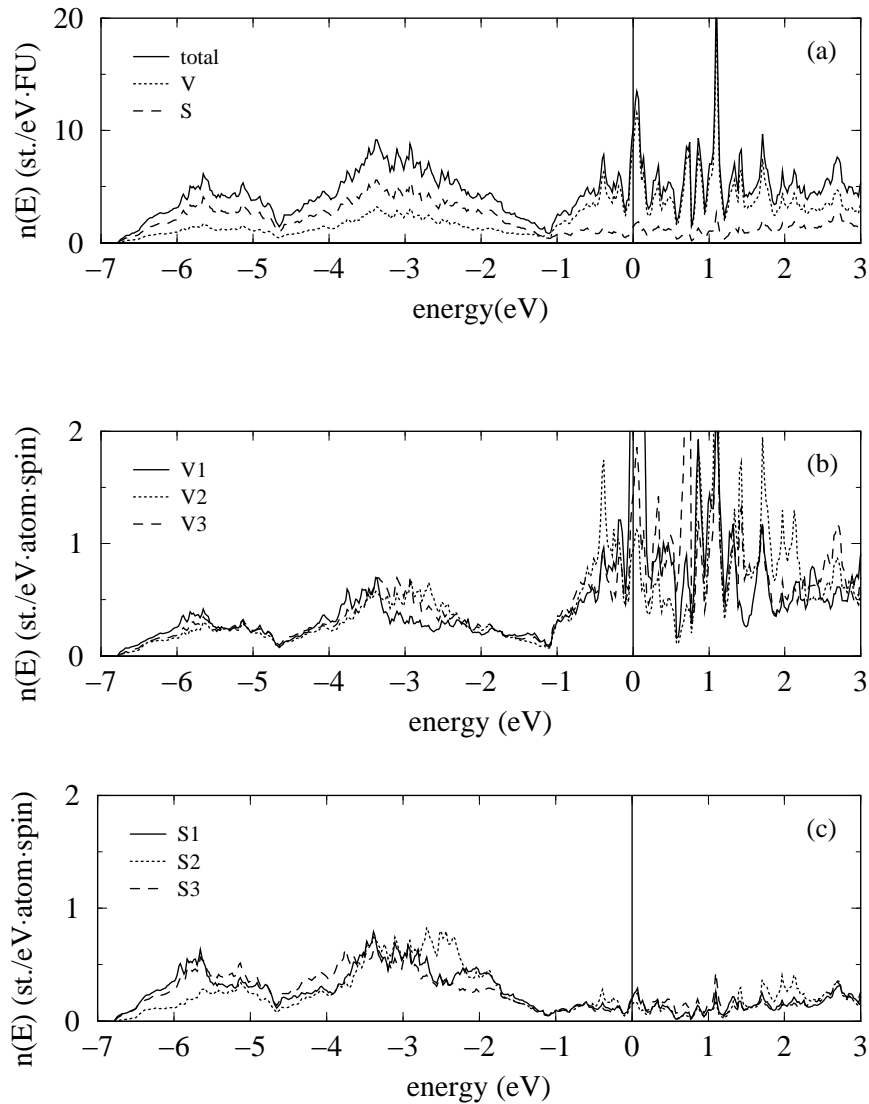


Figure 3. The total and component-resolved DOS $n(E)$ for paramagnetic V_5S_8 . Part (a) compares the total DOS with its V and S contributions. The latter are split in parts (b) and (c) into their contributions coming from the various non-equivalent sites.

4. Results

4.1. The paramagnetic state

To supply a reference system for the discussion of antiferromagnetically ordered V_5S_8 , the electronic properties of paramagnetic V_5S_8 have been determined as well. The corresponding calculated density-of-states (DOS) curves are shown in figure 3, together with the partial contributions of the constituents. The numerical results for the effective charges Q within the various Wigner–Seitz spheres of the components and the DOS $n(E_F)$ at the Fermi energy E_F are summarized in table 2.

Table 2. Numerical results of the band-structure calculations for paramagnetic V_5S_8 . The charge Q gives the deviation from neutrality within a Wigner–Seitz sphere. The empty spheres introduced are labelled E. The component-resolved DOS at the Fermi level $n_\alpha(E_F)$ is given in states eV^{-1}/atom while the total DOS is given per FU.

	Q (e)	$n(E_F)$ (states eV^{-1})
V1	−0.093	7.324
V2	−0.144	1.877
V3	−0.139	2.808
S1	−0.111	0.396
S2	−0.516	0.293
S3	−0.233	0.367
E1	0.961	0.058
E2	0.926	0.059
Total		19.714

Not shown in figure 3 is a low-lying band at around -10 eV below the Fermi energy E_F that has nearly exclusively S s character. Between -6.6 eV and -1.0 eV the DOS is dominated by S p states but with a strong covalent mixing with V 3d states. From -1.0 eV to 3.3 eV the DOS has mainly V d character, but the contribution from S p states cannot be neglected. The nearly octahedral coordination of all V atoms with the S atoms causes a ligand-field splitting of the V d states into two sub-bands that can be reasonably well classified as t_{2g} and e_g bands.

Table 3. Numerical results of the band-structure calculations for antiferromagnetic V_5S_8 . The charge Q gives the deviation from neutrality within a Wigner–Seitz sphere. The component and spin-resolved DOS at the Fermi level $n_\alpha(E_F)$ is given in states $eV^{-1}/(\text{atom spin})$ while the total DOS is given per FU.

	Q (e)	$n_\uparrow(E_F)$ (states eV^{-1})	$n_\downarrow(E_F)$ (states eV^{-1})	μ_{spin} (μ_B)
V1	−0.089	2.162	0.178	1.444
V2	−0.146	0.891	0.719	0.009
V2 ₀	−0.146	0.807	0.807	0.000
V3 _A	−0.141	1.051	0.870	0.246
V3 _B	−0.141	1.379	0.877	0.010
S1 _A	−0.108	0.157	0.104	
S1 _B	−0.108	0.156	0.100	
S2 _A	−0.517	0.132	0.103	
S2 _B	−0.517	0.112	0.117	
S3 _A	−0.233	0.173	0.111	
S3 _B	−0.233	0.174	0.114	
E1 _A	0.961	0.028	0.022	
E1 _B	0.961	0.025	0.025	
E2	0.926	0.025	0.022	
Total			12.016	

4.2. The antiferromagnetic state

For the spin-polarized calculations for antiferromagnetic V_5S_8 , the spin configuration as specified by Funahashi *et al* [9] for their sample 2 has been assumed (see figure 2). The

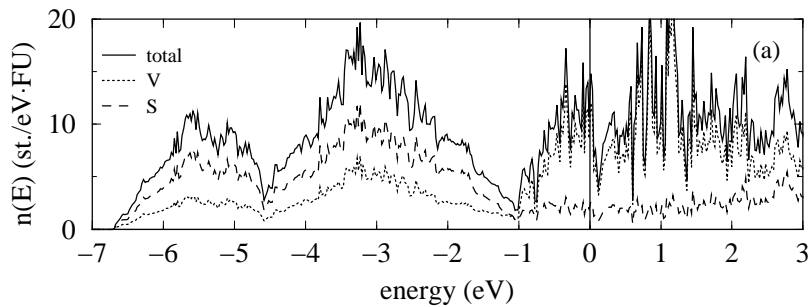


Figure 4. The total and component-resolved DOS $n(E)$ for antiferromagnetic V_5S_8 , as for figure 3. In parts (b) and (c) the spin-resolved DOS curves for V and S are shown, respectively. These give, for the left-hand cell of the antiferromagnetic unit cell (see figure 2), the DOSs for the various sites for spin-up and spin-down character. For the second half of the unit cell, the spin character is just reversed. Because the curves for corresponding subtypes, e.g. $V3_A$ and $V3_B$, are very similar, their average is shown.

corresponding calculated total and partial DOSs of V_5S_8 are shown in figure 4. The numerical results for the charges Q , the DOS $n(E_F)$ at the Fermi energy E_F and the magnetic moments within the Wigner–Seitz spheres are summarized in table 3. Comparing the various DOS curves in figures 3 and 4, one notes that for the antiferromagnetic state essentially the same sequence of S s, S p and V d bands occurs as for the paramagnetic case. However, in contrast to this, the states with V1 d character now show a pronounced exchange splitting of about 0.66 eV.

As a consequence, the relatively high DOS for the paramagnetic case, namely 19.714 states eV^{-1}/FU , is strongly reduced for the antiferromagnetic case, to 12.016 states eV^{-1}/FU . Without doubt, this contributes considerably to the lowering of the total energy of the antiferromagnetic state with respect to the paramagnetic one, which is found to amount to 6 mRyd/FU

5. Discussion

As mentioned above, there are a great variety of magnetic behaviours shown by 3d-transition-metal chalcogenides. The susceptibility of the titanium sulphides, for example, is weakly temperature dependent. In contrast to this, the susceptibility of the chromium sulphides follows a Curie–Weiss law. Finally, the magnetic susceptibility of the vanadium chalcogenides has in general a large temperature-independent component. However, in some cases these may also possess a temperature-dependent part which follows a Curie–Weiss law. These magnetic properties seem to indicate a change from an itinerant to a localized behaviour of the transition-metal sulphides through the 3d series. Even for the latter situation, band-structure calculations allow one to achieve an appropriate description of their magnetic properties. This has been demonstrated for example by Kübler *et al* [14] for the case of Heusler alloys, which were considered in the past to be ideal local moment systems.

In line with this experience, the calculated moment of V1 ($1.44 \mu_B$) for the antiferromagnetic state of V_5S_8 is found to be in very good agreement with that determined by neutron scattering experiments ($1.5 \mu_B$ [9]). For this site, the spin-up d states are found to be partly occupied, while the spin-down d states are nearly empty. The corresponding d

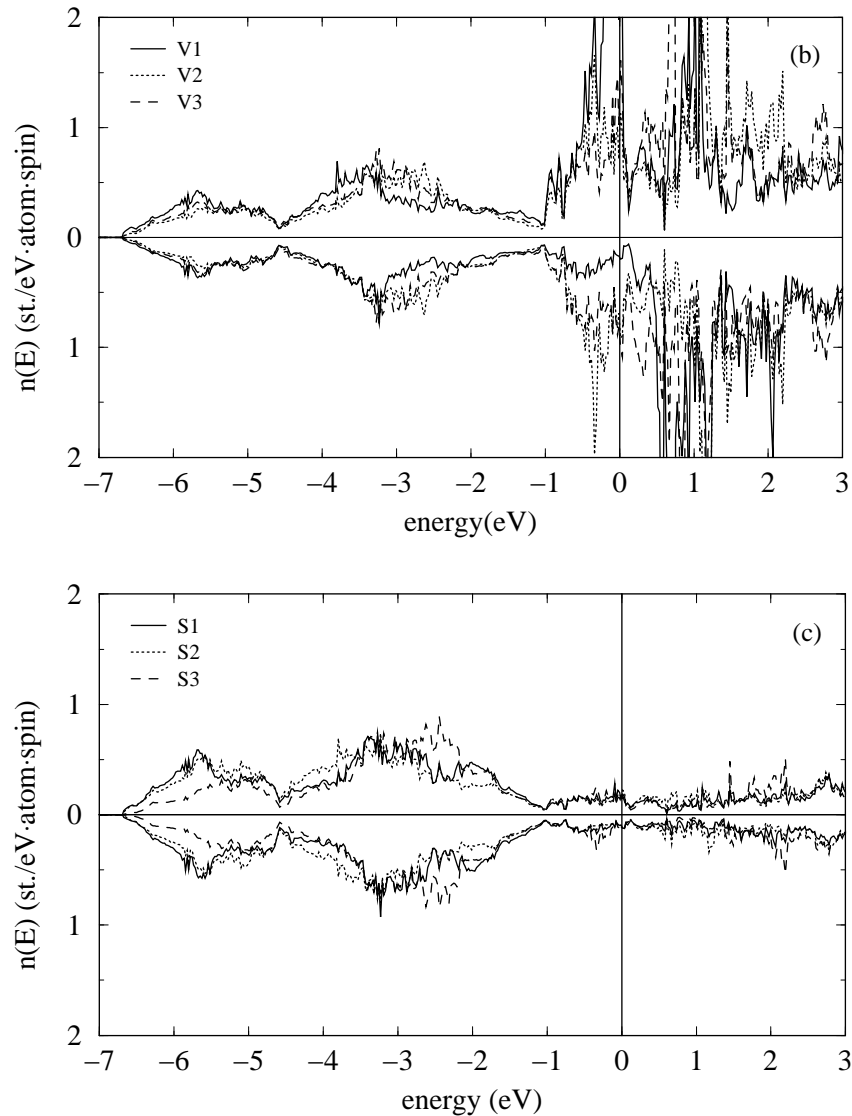


Figure 4. (Continued)

bandwidths (around 4.72 eV) are very similar to those for the V2 and V3 sites, indicating a comparable degree of delocalization. On the other hand, one can see in figure 3 and table 2 that the DOS at the Fermi level $n(E_F)$ is higher for V1 than for V2 and V3 by more than a factor of 2. This difference in $n(E_F)$ for the various V sites can be traced back to the spatial structure of V_5S_8 . In contrast to the case for the planes containing the sites V2 and V3, the distance between the V1 sites within the other planes is quite large. Accordingly, one has a weak overlap for the in-plane-oriented d orbitals of adjacent V1 sites. In fact, an analysis of the DOS around the Fermi energy shows that the peak for the V1 site stems from a band with weak dispersion and predominantly V1 $d_{x^2-y^2}$ character. Using the Stoner exchange–correlation integral I for pure V (0.35 eV) [15], one finds for

the Stoner enhancement factor

$$S = \frac{1}{1 - n(E_F)I}$$

the values -0.64 , 2.9 and 50 for the three different V sites. This means that the Stoner criterion for the spontaneous formation of a spin magnetic moment is fulfilled locally only for the V1 site but not for the others. In accordance with this, the magnetic moment for the magnetically ordered state is by far highest for site V1 ($1.44 \mu_B$). Nevertheless, there is also an appreciable moment found for site V3, which in the paramagnetic state is close to a magnetic instability. For the site V2, finally, the Stoner enhancement factor S is close to that of pure V (2.34 [15]) and accordingly a negligible magnetic moment is found in the spin-polarized calculation.

These considerations, based on the Stoner criterion, obviously give a clear hint that the paramagnetic state of V_5S_8 is unstable against a magnetic ordering. However, they do not allow one to predict whether a ferromagnetic or an antiferromagnetic ordering occurs. The latter question can be answered only on the basis of an additional calculation of the total energy for the ferromagnetic state. Corresponding calculations have been done, leading to the result that the antiferromagnetic state is indeed energetically more favourable. However, the energetic difference is rather small because the magnetic moments on the various V sites for the ferromagnetic state are very similar to those for the antiferromagnetic state.

As mentioned above, NMR measurements have been done on V_5S_8 by various groups [3–6]. These investigations have been done for the paramagnetic state above the Néel temperature (28.5 K). Within the more recent work of Silbernagel *et al* [4], the NMR signals of all three inequivalent sites could be recorded for a wide range of temperatures (90 to 573 K). For all cases the temperature dependence of the resonance position was found to stem primarily from a contribution to the Knight shift K that behaves in a Curie–Weiss-like manner. For the signal that has been assigned by Silbernagel *et al* [4] to the site V1, the corresponding Knight shift K varies between -6.5 and -1.7% for the above-mentioned temperature range. This finding seems to indicate that the spin magnetic moment of V1 for the antiferromagnetic phase is essentially preserved above the Néel temperature. This can be seen by using the corresponding calculated moment for V1 ($1.44 \mu_B$) and assuming a Curie–Weiss-like temperature variation for its component along the direction of the external magnetic (NMR) field. With the core-polarization hyperfine field taken from calculations for pure V (-88 kG/d electron) [16]), one gets a variation of K between -5.75 and -0.76% for the above-mentioned temperature range. Keeping in mind that this simple consideration neglects the Van Vleck contribution of the d electrons as well as the direct contribution of the s electrons to K , the agreement with experiment is rather satisfying and supports the assumption made above.

Unfortunately, the situation is less clear-cut for the other two V sites. First of all one has to note that the two experimental NMR groups who studied the V resonance in V_5S_8 so far gave different assignments for the two remaining signals, to the sites V2 and V3. If one were to assume also for site V3 that the spin magnetic moment persists above the Néel temperature, one would expect a temperature dependence of its Knight shift similar to that for V1—except that its magnitude should be reduced by the ratio $\mu(V3)/\mu(V1)$. However, this applies to neither of the remaining two experimental signals [4]. For that reason, one may conclude that, in contrast to that of V1, the relatively large moment for V3 does not persist above the Néel temperature.

To get more insight into the NMR properties, one would have to perform corresponding theoretical investigations within the framework of linear response theory [16, 17]. However, this is beyond the scope of the present study.

6. Summary

Self-consistent band-structure calculations have been performed for V_5S_8 in the paramagnetic, ferromagnetic and antiferromagnetic states. On the basis of the Stoner criterion, it was shown that V_5S_8 should be magnetic with the highest spin magnetic moment occurring for V1. This was confirmed by spin-polarized calculations which found, in agreement with experiment, the antiferromagnetic phase to be the most stable one. Comparison with experimental NMR data gave an indication that the spin magnetic moment of V1 persists above the Néel temperature giving rise to a Curie–Weiss-like temperature dependence for the global spin susceptibility as well as the Knight shift for the various V sites.

Acknowledgment

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