Vanadium doping in $YB_{44}Si_{1.0}$

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Abstract. Vanadium doping in yttrium boron-rich boride; $YB_{44}Si_{1.0}$, is investigated. Vanadium atoms occupy two sites. First, newly discovered site with site occupancy of approximately 3% is far from yttrium atoms and is coordinated "tetrahedrally" by three boron icosahedra and one $B_{12}Si_3$ polyhedron. Another is Si/V mixed-occupation site with site occupancy of ~ 63/6.2 %; it is close to yttrium atoms and is tetrahedrally coordinated by four boron icosahedra. Chemical formula determined from the structure analysis is $Y_{0.96}V_{0.062}B_{41.2}Si_{0.93}$. Magnetic susceptibility of V-doped $YB_{44}Si_{1.0}$ was measured from 2 K to 300 K. The vanadium doping in $YB_{44}Si_{1.0}$ did not result in superconductivity.

1. Introduction

There have been expectations of superconductivity and improved thermoelectric properties of icosahedral boron-rich borides doped by metal elements. The doping of metal elements into β-boron has extensively been investigated [1-3]. It is well known that vanadium doping into β-boron with only a few atm% causes a metal-like high electrical conductivity. Rare-earth boron-rich borides have higher electrical conductivity than β-boron so that metal doping may cause a metallic conductivity easier than β-boron.

$YB_{44}Si_{1.0}$ [4] is unique in rare-earth boron-rich borides or boron-rich metal borides. Partial occupancy of rare-earth sites or metal sites is common for the icosahedral boron cluster structure of boron-rich borides. For example, the occupancy of the Y-site in YB_{66} is only about 50% [5]. Mg and Al site occupancies in a well-known boron-rich boride $MgAlB_{14}$ are only 60-70%. On the other hand,

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the 100% site-occupancy was observed for the Y-site in $YB_{44}Si_{1.0}$ [6], which is the only case reported up to now.

$YB_{44}Si_{1.0}$ has an orthorhombic crystal structure (space group: *P*bam (No.55)) with lattice constants of a = 16.674(1) Å, b = 17.667(1) Å, c = 9.5110(7) Å [6]. The boron framework structure of $YB_{44}Si_{1.0}$ is made of five structurally independent icosahedra I1-I5 and one $B_{12}Si_3$ polyhedron. The Y-sites arrange along the *c*-axis like a ladder, as shown in figure 1 where only icosahedra I2, I4 and Y atoms are depicted for clarity.

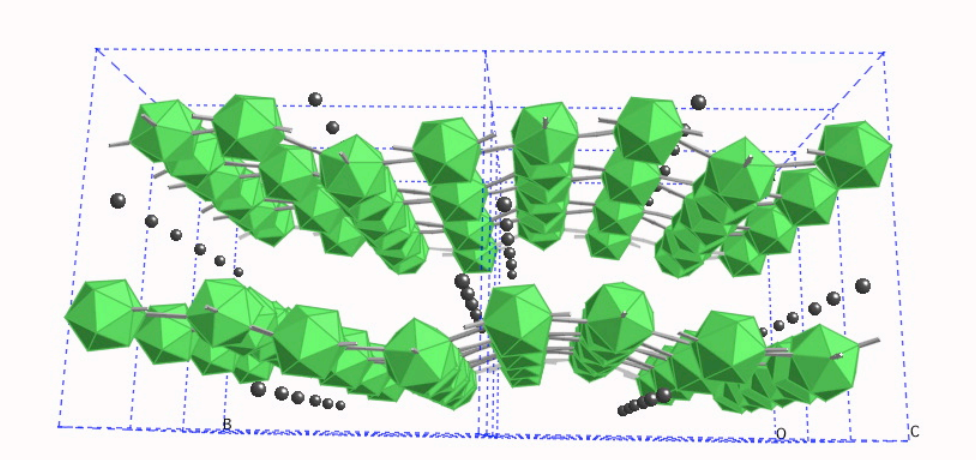


Figure 1. Arrangement of yttrium atoms (black) in $YB_{44}Si_{1.0}$. The viewing direction is close to [001]. Only icosahedra I2 and I4 are depicted for clarity.

The Y-Y distances along the *c*-axis are 4.368 and 5.143 Å, and the Y-Y distance within the *a*-*b* plane is only 3.916 Å. The ladder-like arrangements of the Y-sites are separated ~10 Å. All Y-Y distances in the ladder are shorter than Y-Y distance in YB_{12} (5.303 Å); the latter shows metallic conductivity although the boron cluster in YB_{12} is not the icosahedron but a cubo-octahedron. It is expected that addition of valence electrons by doping with a transition metal may cause metallic conduction due to increasing interaction between the Y sites in the ladder.

In this paper, we describe V-site assignment in the V-doped $YB_{44}Si_{1.0}$. We also measured the magnetic susceptibility to probe a possible superconducting behavior.

2. Experimental details

Single crystals of V-doped $YB_{44}Si_{1.0}$ [4] were grown by the floating zone (FZ) method using a 4-mirror, xenon-lamp image furnace (Crystal Systems Inc., Japan). Raw powders with a desirable composition were synthesized for the crystal growth by reacting powders of YB_4, amorphous boron, VB_2 and Si under vacuum, using a carbon-free crucible system at temperatures ~1700 °C for several hours. A compacted green rod of the synthesized powder was sintered under the same condition as used for the reaction. The obtained rod had an apparent density of only about 60% because of poor sinterability of rare-earth boron-rich borides that have a strong covalent character. Hot zone pass technique was applied to consolidate the feed rod [7].

The molten zone composition should be controlled in the FZ growth because vanadium concentration is different in the crystal and in the molten zone. After the partition coefficient of vanadium at the growth interface was experimentally determined, a pellet with a suitable composition was prepared and set at the place of the initial molten zone. Then the floating zone passage was carried out through the feed rod.

Single-crystal X-ray diffraction (XRD) data were collected using a CCD- detector diffractometer (Bruker SMART APEX, Germany) with graphite-monochromated MoKα radiation. The intensity data were corrected for Lorentz and polarization effects. The absorption correction applied to the collected data was based on multiple scans. A single-crystal specimen for XRD was obtained by cracking the central part of the FZ-grown crystal. The program SHELXL-97 [8] was used for refinement. The crystal structure was visualized with the program CrystalMaker [9]. Crystallographic and data collection parameters are given in table. 1.

To determine chemical composition of the specimens, electron probe microanalysis (EPMA) was carried out in wavelength-dispersive mode using JEOL JXA-8500F instrument. Standard samples used for Y and B, V and Si are, YB_6 crystal, V metal and Si crystal, respectively.

Magnetic susceptibility was measured using a SQUID magnetometer from 2 to 300 K under a magnetic field of 50 G.

3. Results and discussion

The floating zone passage was carried out for the rod with composition of $YVB_{44}Si_{1.0}$. The obtained rod was so conductive that a spark erosion cutter could be used to slice the rod. Metallographic observation indicated that the central part of the rod is a single-phase crystallite, though it had many cracks. Powder XRD suggested that the central part is a single phase of V-doped $YB_{44}Si_{1.0}$; however, wet chemical analysis indicated much higher V content (2.4 wt%) than expected (0.54 wt%). Thus, a small amount of VB_2 could be present as inclusions even in the central part. Weak XRD peaks of VB_2 were not detected, but they might be buried under a complex XRD spectrum of V-doped $YB_{44}Si_{1.0}$ [4]. The outer part of the zone-passed rod apparently contained several phases. EPMA yielded nearly 100% for the total of the Y, V, B and Si contents, which supports reliability of EPMA measurement. The measured values are 14.6±0.1, 0.540±0.006, 79.7±0.1 and 5.16±0.20 wt%, respectively, where the total was normalized to 100%. Thus, as indicated in table 1, the chemical composition is $YV_{0.065}B_{44.9}Si_{1.12}$. The extra phase in the outer part of the zone-passed rod is mainly VB_2.

Table 1. Crystallographic and data collection parameters.

Crystal	$YV_{0.065}B_{44.9}Si_{1.12}$ [a]
Crystal system	Orthorhombic
Space group	*P*bam (No.55)
a (Å)	16.643(2)
b (Å)	17.625(2)
c (Å)	9.495(1)
V (Å^3)	2785.2
Chemical composition	$Y_{0.96}V_{0.062}B_{41.2}Si_{0.93}$ ($YV_{0.065}$ $B_{43.0}Si_{0.97}$) [b]
Z	8
D_x (g/cm^3)	2.674
Applied Radiation	Mo$K\alpha$
μ for Mo$K\alpha$ (cm^{-1})	42.62
Crystal dimensions (mm)	0.5 × 0.4 × 0.25
Reflections measured	22,962 reflections -23 h 22 -18 k 24 -13 l 11
$2\theta_{max}$ (°)	62.21°
Structure refinement program	SHELXL97
*R*1	0.030 ($F_o>4\sigma(F_o)$, for 3758 F_o), 0.035 (all F_o, for 4313 F_o)
wR2	0.087
Number of variables	221

[a] Obtained by EPMA chemical analysis. The chemical composition is normalized for Y.
[b] Obtained by structure analysis. The composition in the parenthesis is normalized for Y.

Structure analysis was carried out using the $YB_{44}Si_{1.0}$ crystal structure [6] as an initial model where 58 independent atoms (one Y site, 53 B sites, 3 B/Si mixed occupation sites and one Si site) have been reported. Almost all sites were reproduced except for two interstitial boron sites, and only one new site was found. All atom coordinates, occupancies and temperature factors are summarized in table 2.

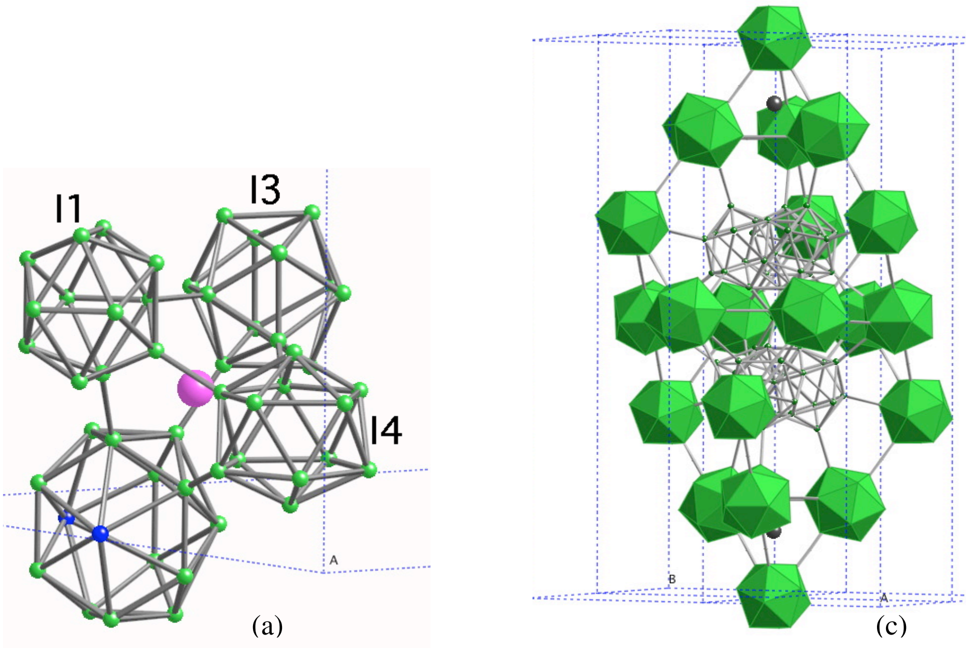
Table 2. Structural data for $YV_{0.065}\,B_{43.0}Si_{0.97}$

Atom	Site	*x*	*y*	*z*	Occ.	U_{eq}
B1.1	8*i*	0.9364(1)	0.5492(1)	0.5930(2)	1	0.0070(4)
B1.2	8*i*	0.9657(1)	0.4613(1)	0.6563(2)	1	0.0072(4)
B1.3	4*g*	0.9058(2)	0.4715(2)	0.5	1	0.0068(5)
B1.4	4*g*	0.9852(2)	0.4080(2)	0.5	1	0.0081(5)
B2.1	8*i*	0.7327(1)	0.4906(1)	0.5975(2)	1	0.0069(4)
B2.2	8*i*	0.7104(1)	0.3281(1)	0.5953(2)	1	0.0069(4)
B2.3	8*i*	0.6668(1)	0.4147(1)	0.6634(2)	1	0.0072(4)
B2.4	8*i*	0.7744(1)	0.4004(1)	0.6583(2)	1	0.0067(4)
B2.5	4*g*	0.6295(2)	0.3703(2)	0.5	1	0.0070(5)
B2.6	4*g*	0.6382(2)	0.4690(2)	0.5	1	0.0064(5)
B2.7	4*g*	0.8108(2)	0.4451(2)	0.5	1	0.0064(5)
B2.8	4*g*	0.7979(2)	0.3461(2)	0.5	1	0.0076(5)
B3.1	8*i*	0.8795(1)	0.1879(1)	0.5973(2)	1	0.0071(4)
B3.2	8*i*	0.5357(1)	0.2422(1)	0.5944(2)	1	0.0069(4)
B3.3	8*i*	0.9826(1)	0.1773(1)	0.6638(2)	1	0.0066(4)
B3.4	8*i*	0.9351(1)	0.2692(1)	0.6584(2)	1	0.0069(4)
B3.5	4*g*	0.9501(2)	0.1249(2)	0.5	1	0.0070(5)
B3.6	4*g*	0.8728(2)	0.2757(2)	0.5	1	0.0082(5)
B3.7	4*g*	0.9683(2)	0.3145(2)	0.5	1	0.0068(5)
B3.8	4*g*	0.5420(2)	0.3279(2)	0.5	1	0.0067(5)
B4.1	8*i*	0.7005(1)	0.1544(1)	0.5879(2)	1	0.0072(4)
B4.2	8*i*	0.6313(1)	0.0978(1)	0.6783(2)	1	0.0076(4)
B4.3	8*i*	0.6157(1)	0.1968(1)	0.6739(2)	1	0.0079(4)
B4.4	8*i*	0.7108(1)	0.2413(1)	0.6761(2)	1	0.0072(4)
B4.5	8*i*	0.7903(1)	0.1674(1)	0.6835(2)	1	0.0071(4)
B4.6	8*i*	0.7373(1)	0.0745(1)	0.6822(2)	1	0.0066(4)
B4.7	8*i*	0.6740(1)	0.0668(1)	0.8368(2)	1	0.0080(4)
B4.8	8*i*	0.5974(1)	0.1447(1)	0.8322(2)	1	0.0076(4)
B4.9	8*i*	0.6511(1)	0.2377(1)	0.8304(2)	1	0.0073(4)
B4.10	8*i*	0.7616(1)	0.2218(1)	0.8361(2)	1	0.0075(4)
B4.11	8*i*	0.7720(1)	0.1169(1)	0.8448(2)	1	0.0087(4)
B4.12	8*i*	0.6886(1)	0.1592(1)	0.9155(2)	1	0.0074(4)
B5.1	8*i*	0.6149(1)	0.4080(1)	0.8356(2)	1	0.0076(4)
B5.2	8*i*	0.6065(1)	0.3126(1)	0.9059(2)	1	0.0075(4)
B5.3	8*i*	0.5256(1)	0.4551(1)	0.9059(2)	1	0.0077(4)
B5.4	8*i*	0.5173(1)	0.3591(1)	0.8361(2)	1	0.0075(4)
B5.5	4*h*	0.9619(2)	0.1117(2)	1	1	0.0084(5)
B5.6	4*h*	0.6679(2)	0.3814(2)	1	1	0.0114(6)
B5.7	4*h*	0.6203(2)	0.4682(2)	1	1	0.0087(5)
B5.8	4*h*	0.5101(2)	0.3014(2)	1	1	0.0104(5)
B6.1	8*i*	0.8315(1)	0.3861(1)	0.8062(2)	1	0.0086(4)
B6.2	8*i*	0.8530(1)	0.4755(1)	0.9072(2)	1	0.0101(4)
B6.3	8*i*	0.9297(1)	0.4216(1)	0.8067(2)	1	0.0075(4)
B6.4	8*i*	0.9151(1)	0.3222(1)	0.8067(2)	1	0.0082(4)
B6.5	8*i*	0.5012(1)	0.1350(1)	0.9052(2)	1	0.0088(4)
B6.6	8*i*	0.8274(1)	0.2923(1)	0.9063(2)	1	0.0108(4)
Si/B6.7	4*h*	0.7786(1)	0.3865(1)	1	0.506/0.494	0.0071(4)
Si/B6.8	4*h*	0.4430(1)	0.2208(1)	1	0.354/0.626	0.0069(4)
Si/B6.9	4*h*	0.9654(1)	0.4623(1)	1	0.364/0.636	0.0097(5)
B7.1	8*i*	0.8915(3)	0.3748(4)	0.6173(7)	0.32(1)	0.0052(18)
B7.3	4*g*	0.9566(2)	0.0210(2)	0.5	1	0.0074(5)

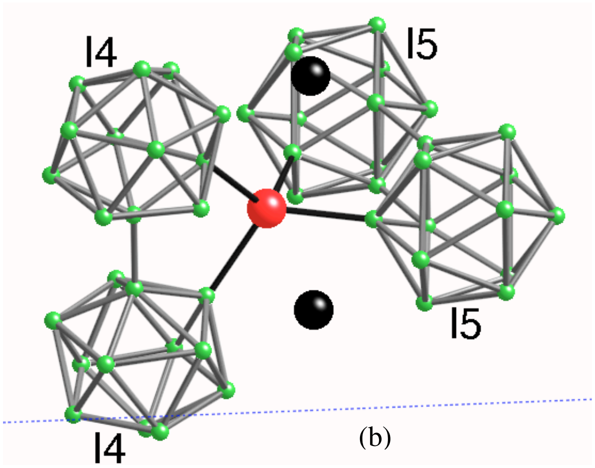
B7.4	4*g*	0.5761(7)	0.1563(6)	0.5	0.34(1)	0.019(3)
B7.5	4*g*	0.6432(8)	0.2494(8)	0.5	0.30(1)	0.024(4)
B7.6	4*g*	0.7570(7)	0.2615(7)	0.5	0.24(1)	0.006(3)
Y	8*i*	0.89626(1)	0.05193(1)	0.73011(2)	0.955(2)	0.0068(1)
V1	8*i*	0.5118(5)	0.1410(5)	0.3094(9)	0.031(2)	0.0012(26)
Si/V	4*h*	0.8439(1)	0.0798(1)	1	0.63/0.062	0.0055(2)

* Occ. is occupancy and $U_{\mathrm{eq.}}$ is equivalent temperature factor. Each boron atom is designated by a set of two number. The first number (1-5) indicates the number of icosahedron to which the boron atom belongs. The number 6 designates a polyhedron $B_{12}Si_3$ and the number 7 indicates that they are interstitial boron atoms.

The new site is tetrahedrally coordinated by the icosahedra I1, I3, I4 and the $B_{12}Si_3$ polyhedron, as shown in figure 2(a). This tetrahedral coordination is very similar to the so-called A_1-site of β-boron, as shown in figure 2(c). The doped vanadium in β-boron occupies the A_1-site. Thus, the new site is assigned as the vanadium site V1. The distances between the V1 site and the surrounding B atoms range from 1.986 Å to 2.101 Å.



(a) (c)



(b)

Fig. 2. Tetrahedrally coordinated V-sites in the $YB_{44}Si_{1.0}$ crystal structure (a and b) and in the β-boron crystal structure (c). (a) V1 site (violet) is coordinated by the icosahedra I1, I3, I4 (left to right) and the $B_{12}Si_3$ polyhedron (bottom). (b) Si/V mixed occupancy site (red) is coordinated by the two icosahedra I4 (left two) and two icosahedra I5 (right two). Y atoms (black) locate 2.751 Å apart above and below the Si/V site. Lines between V ion and icosahedra are drawn to show the tetrahedral coordination relation, (c) Vanadium atom (black) occupies *A1* site of β-boron crystal structure, which is tetrahedrally coordinated by four icosahedra.

However, the site occupancy is only about 3%, which cannot explain the measured vanadium content. Another V-site is required. The only possibility is the site previously assigned as the interstitial Si. It is also tetrahedrally coordinated by 4 icosahedra, although the configuration is different from that shown in figures 2(a) and (c), where the V-sites locate at the center of a cage formed by 4 polyhedra (I1, I3, I4 and $B_{12}Si_3$) and 4 icosahedra, respectively. On the other hand, the interstitial Si site is directly linked to each apex boron atom of 4 icosahedra. We expected that the vanadium atom occupies the interstitial Si site because Si and V tend to share a site such as the A_I-site of β-boron. Thus, the Si site was assigned as the vanadium site that is shown in figure 2(b). The site occupancy reaches ~50% if assuming that only V occupies the site, which is too high compared with the measured V content of 0.54 wt%. It is possible that V and Si share the site, however, introduction of partial and mixed occupancy to the site was unsuccessful. This is because there is little difference of R values between the case where the site is solely occupied by Si and the case where the site is solely occupied by V. The structure analysis did not converge when the parameters of simultaneous and partial occupation of the site were introduced. To solve this problem, we fixed vanadium occupancy at the site to coincide to the measured V content. The final Si/V ratio is approximately 63/6.2%. The distances from the Si/V site to each boron atom are 2.008 Å for I4 and 2.043 Å and 2.055 Å for I5, respectively.

The final $R1$ values are 3.0% with 221 parameters for 3758 independent reflections [$F_o > 4\sigma(F_o)$] and 3.5% for all 4313 independent reflections. The calculated chemical composition is $Y_{0.96}V_{0.062}B_{41.2}Si_{0.93}$ ($YV_{0.065}B_{43.0}Si_{0.97}$), which agrees relatively well with the measured chemical composition $YV_{0.065}B_{44.9}Si_{1.12}$.

It is difficult to discuss the small difference of Y content as compared to the previous undoped $YB_{41}Si_{1.2}$ [6] in relation to the V doping because the site occupancies obtained by the structure analysis usually include ±5% error. In the previous structure analysis, we have fixed the site occupancy of Y as 100 % because the calculated values were always very close to that. Decrease of the Si content is due to the replacement of the interstitial Si by V.

The Si/V site is characterized by its closeness to the Y site as shown in the figure, where the distance between these sites is only 2.751 Å. This distance is acceptable in metallic borides. For example, Mo – Mo distance in $YMoB_4$ is only 2.51 Å. Because of the small number of V atoms in the Si/V site, the V atoms are probably not effective to assist the interaction between Y atoms in the ladder. Relation between the V1 and Si/V sites and the Y sites is shown in figure 3, where all the V1 and Si/V sites in the range are depicted ignoring the site occupancy. Actually, only one V atom occupies the V1 sites (total 24 sites), and one V atoms and 15 Si atoms occupy the Si/V sites (total 24 sites) in the range, remaining sites are vacant.

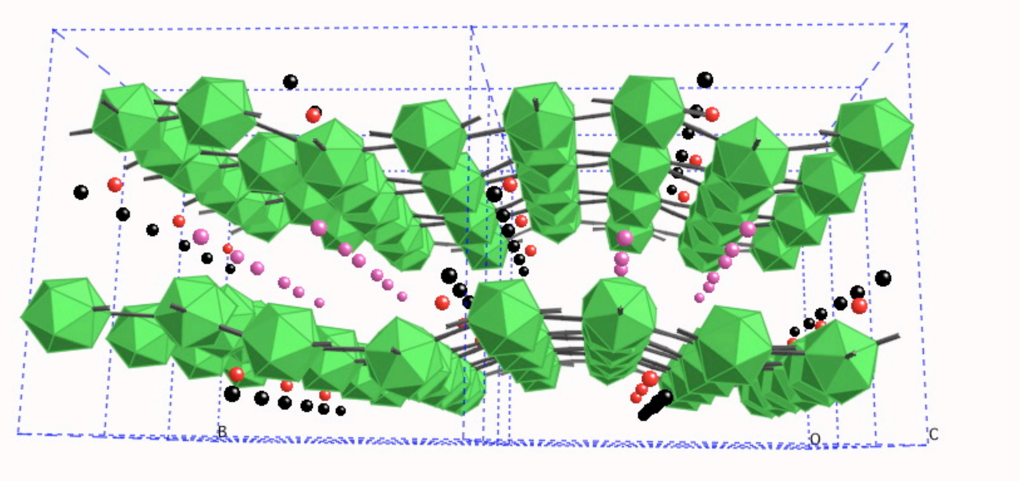


Figure 3. Correlation between the V1 (violet) and Si/V sites (red) and the Y site (black) in $YB_{44}Si_{1.0}$. The viewing direction is close to [001]. Only the icosahedra I2 and I4 are depicted.

In expectation of superconductivity, magnetic susceptibility of the V-doped $YB_{44}Si_{1.0}$ sample was measured. Before the measurement, the pulverized sample was washed by hydrochloric acid to remove VB_2 that may remain in the sample. Superconductivity was not observed in this temperature range as shown in figure 4. The susceptibility is paramagnetic which could indicate a contribution from a Pauli paramagnetic term, although the value of 3.3 x 10^{-7} emu/g at 300 K is small. The increase at low temperatures can be attributed to a minor impurity.

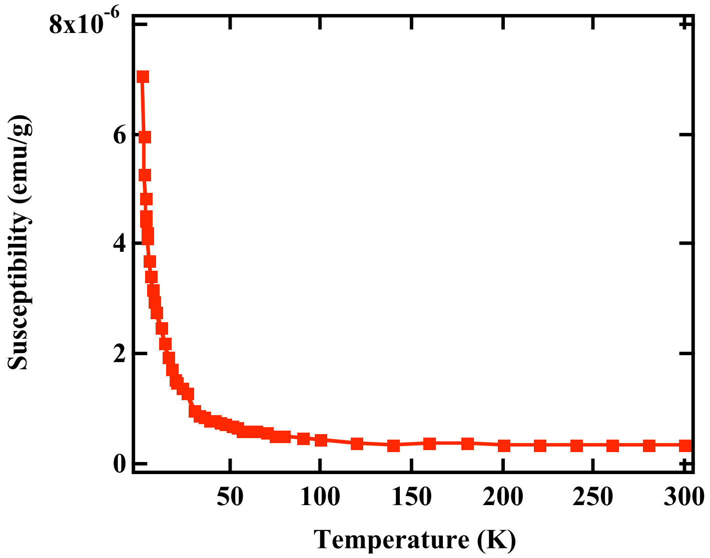


Figure 4. Temperature dependence of magnetic susceptibility of V-doped $YB_{44}Si_{1.0}$.

Relatively low electrical resistivity of 0.009 cm at room temperature was measured. However, it could be ascribed to the VB_2 inclusions remained in the large sample ($1{\times}1{\times}10$ mm^3) used for the measurement, although the sample was cut from the central single-crystal region. The temperature dependence of resistivity was semiconducting.

4. Conclusions

Vanadium doping in $YB_{44}Si_{1.0}$ was investigated. A vanadium site V1 and a mixed occupancy Si/V site were found, the V1 site is a new site and the Si/V site was assigned to the interstitial Si site in the undoped $YB_{44}Si_{1.0}$. Chemical composition obtained by the structure analysis is $Y_{0.96}V_{0.062}B_{41.2}Si_{0.93}$ ($YV_{0.065}$ $B_{43.0}Si_{0.97}$). The obtained V content must be the maximum equilibrium content of $YB_{44}Si_{1.0}$ because the crystal was melt-grown in equilibrium, under excess V condition. The V doping in $YB_{44}Si_{1.0}$ does not cause semiconductor-metal transition.

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