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Synthesis and Characterization of a New Ternary Nitride: Ca_3VN_3

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ABSTRACT

We have synthesized a new ternary nitride, Ca_3VN_3, from the binary nitrides at high temperature. The refined structure was solved in the $P2_1/m$ space group with lattice constants a=6.717(2), b=5.064(2), c=6.720(3), β=78.88(3), Z=2, and R=3.2%, R_w=3.7%. The structure is related to the recently reported A_3MN_3 compounds (1) with sheets of $[VN_3]^{6-}$ trigonal planar units and calcium ions. Ca_3VN_3 is insulating with V^{3+} in the low-spin state, S=0.

Introduction

Recently we have reported the synthesis and properties of alkaline earth-transition metal nitrides (1, 2, 3). A new structure type was observed in Ca_3CrN_3 (1), which consists of sheets of trigonal planar $[CrN_3]^{6-}$ units separated by Ca ions. This was the first solid state example of a transition metal in a trigonal planar environment of nitrogen atoms. The low Cr site symmetry (C_{2v}) and high covalency of the Cr-N bonding leads to a low spin Cr^{3+} (S=1/2) state. Ca_3CrN_3 is the only Cr^{3+} compound known to be low spin. Since our report of Ca_3CrN_3, more alkaline earth transition metal nitride structures have been reported to contain this $[MN_3]^{6-}$ unit; for example, $Ba_3(Sr_3)FeN_3$ (4), and $Ca_6Fe(Ga)N_5$ (5). Although none of these structures are isotypic, they share a common structural feature: planes of $[MN_3]^{6-}$ anions separated by alkaline earth cations. However, magnetic properties of these compounds were not reported.

We report the synthesis, structure and properties of a new compound, Ca_3VN_3, containing $[VN_3]^{6-}$ anions which are separated by Ca^{2+} ions.

Experimental

Starting Materials. Vanadium nitride was prepared by heating vanadium metal (2N5, -325 mesh) in flowing nitrogen (prepurified by passing through finely divided copper at 150°C and then activated alumina) at 1050°C for 15h. Granules of Ca (2N) were reacted at 1000°C for 2 days in flowing nitrogen (prepurified as above) to yield pure Ca_3N_2. The binary products were identified by X-ray

powder diffraction methods. Since both Ca_3N_2 and Ca_3VN_3 are air-sensitive, all manipulations were carried out in an argon-filled glove box.

Synthesis of Ca_3VN_3. The title compound was prepared as small single crystals by heating Ca granules in a vanadium foil boat to 950°C in 12h under Ar, soaking at 950°C for 18.5h under a backpressure of N_2 which allowed slow diffusion of N_2 into the Ar-filled reaction zone, followed by cooling at 22.5°/h to 500°C, and finally cooling to room temperature in 5h. In order to obtain single crystals of the product, it was imperative that the heat up be under Ar and that the reaction take place slowly by indiffusion of N_2. Crystals were not obtained unless we strictly adhered to this heating schedule. The reaction yielded a distribution of brown needle crystals up to 0.5mm in length which were used in the structure determination. Microprobe analysis of the crystals indicated the presence of Ca and V at a Ca:V ratio of approximately 3.5:1.

The compound was then prepared as a polycrystalline phase by heating a pressed pellet of an intimate mixture of Ca_3N_2 (0.391g, 2.64mmol) and VN (0.172g, 2.64mmol) in a sealed molybdenum tube at 1350°C for 30h. X-ray powder diffraction indicated a nearly pure Ca_3VN_3 with a small amount of unidentified impurity phase. The intensity of the strongest impurity diffraction peak in our best material was 13% as intense as the strongest peak of the majority phase. Other preparative conditions always produced larger quantities of the impurity phase. This product was used for both

magnetic susceptibilty and electrical resistivity measurements.

Structure Determination. Unit cell symmetry and approximate lattice constants were obtained from axial photographs of a brown crystal mounted along the needle axis. A 0.25 x 0.045 x 0.018 mm^3 crystal sealed in a 0.3mm glass capillary under argon was used in the structure determination. Data were collected on Syntex $P2_1$ 4 circle diffractometer using MoKα radiation (0.71069Å) and a graphite monochromator. The unit cell dimensions were refined using 25 independent reflections in the 2θ range 15-25°. An appreciable decay of approximately 25% was observed during data collection according to three check reflections measured every 50 reflections. This decay was monotonic in time and was likely due to the slow decomposition of Ca_3VN_3 in the x-ray beam. The data were scaled appropriately to correct for crystal decomposition using XDISK (6). The choice of space groups was reduced to $P2_1$ and $P2_1/m$ by systematic absences, and the structure was solved in the $P2_1/m$ space group. Refinement in the non-centrosymmetric space group resulted in no significant change in the structure or R factors. An empirical absorption correction was applied (the psi scan) and after averaging symmetry related reflections, 468 unique reflections with $F > 3\sigma(F)$ were used to solve the structure.

The structure determination and refinement were performed using Nicolet SHELXTL Plus (6) software running on a Microvax computer. The function minimized in the least squares refinement was $\Sigma\, w(|F_o|-|F_c|)^2$ with $w=\sigma^{-2}$. Anisotropic refinement of all atoms (43 parameters) converged to R=3.2% and R_w=3.7%. Table I

summarizes data collection parameters. Atomic positions are listed in Table II.

After the structure was solved, the powder patterns taken on a Scintag XDS2000 diffractometer could be indexed. The observed pattern minus the impurity peaks matched that calculated by Lazy Pulverix (7) on the basis of the single crystal data.

Electrical Properties. The resistance of a pellet of Ca_3VN_3 was measured in a small press inside the glove box. The two pistons were electrically insulated from each other, allowing a two-point measurement of the resistance. The resistance determined on a pellet 4.5mm in diameter and approximately 3mm thick was larger than 30MΩ (the upper limit of our measurement apparatus) yielding a lower limit to the resistivity on the order of 10^7Ωcm.

Magnetic Susceptibilty. The magnetic susceptibility of the sample was measured by the Faraday technique as previously described (8). The susceptibility of a polycrystalline sample sealed in a thin walled high purity quartz tube was determined to be field independent at room temperature, indicating no ferromagnetic impurities were present. Figure 1 shows the results of a temperature dependent study between 4K and 300K at a magnetic field strength of 13.6KG.

Results and Discussion

The structure of Ca_3VN_3 (Figure 2) consists of trigonal planar $[VN_3]^{6-}$ anions separated by calcium ions. A view down the unique axis clearly shows the stacking arrangement of the eclipsed units. Neighboring $[VN_3]^{6-}$ anions are displaced by 1/2 in z and the

orientation of the triangle is reversed (Figure 3). Although the 3 V-N bond distances are within 0.016Å of each other, the bond angles reduce the symmetry of the anion to C_{2v}, similar to Ca_3CrN_3. A list of relevant bond distances and angles can be found in Table III.

The average V-N distance (1.83Å) is close to the Cr-N distance in Ca_3CrN_3, indicating multiple metal-nitrogen bonding. Each Ca atom is coordinated by 3 nitrogen atoms and 2 calcium atoms in the same plane, and by 2 nitrogen atoms above and below that plane at 2.54 $\pm$ 0.01Å. The three coordinated nitrogen atoms subtend an angle of 170°, creating a quite asymmetric environment about the central Ca. The in-plane Ca-N distances for each of the three inequivalent Ca's are: Ca(A) 2.443Å, 2.625Å, and 2.634Å; Ca(B) 2.447Å, 2.503Å, and 2.818Å; Ca(C) 2.445Å, 2.494Å, and 2.804Å. The shorter Ca-N distances are comparable to those observed in Ca_3N_2 (2.46Å), Ca_3BiN (2.45Å) (3), and CaNiN (2.50Å) (2). The closest Ca-Ca distance between planar units (3.39Å) is slightly longer than in Ca_3N_2 (3.16Å) (9).

The V-V distances are much too long for any metal-metal interactions (shortest distance 5.06Å from V1 to V3 in Figure 3). As expected from the long V-V distances, Ca_3VN_3 is insulating. The susceptibility can be fit with a simple Curie-Weiss expression

$$\chi_g = \chi_o + C_g/T+\theta$$

and we obtain $\chi_o = 1.24 \times 10^{-7}$emu/g, $C_g = 9.04 \times 10^{-6}$emu/g, and $\theta = 5$K (with a mean square deviation of 2.1%). The small value of C_g indicates that the temperature dependence arises from a

paramagnetic impurity. If the V had a moment appropriate to V^{3+} (S=1), the value of C_g would be 4.70 x 10^{-3}emu/g. We conclude that V in Ca_3VN_3 and in the impurity phase present in the sample must be non-magnetic. Since an unknown impurity is present, a definitive value of χ_o for Ca_3VN_3 can not be determined from this measurement. The S=0 assignment for V^{3+} in Ca_3VN_3 is consistent with the low site symmetry and the low spin configuration in Ca_3CrN_3.

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Supplementary Material

Tables of observed and calculated structure factors (3 pages); table of refined anisotropic thermal parameters (1 page) are available for Ca_3VN_3.

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Table I. Summary of Crystal and Diffraction Data for Ca_3VN_3

space group	$P2_1/m$
Z	2
a, b, c (Å)	6.717(2), 5.064(2), 6.720(3)
β (deg)	78.88(3)
V (Å^3)	224.3(2)
density, calc (g/cm^3)	3.157
T (K) data collection	298
crystal dimensions (mm)	0.25 x 0.045 x 0.018
absorption coeff (mm^{-1})	5.334
2θ max (deg), scan type	55, w-2θ
octants collected	hkl; -h-kl; -hkl; h-kl
x-ray radiation	Mo k-α
monochromator	graphite
measured reflections	1109
observed reflections[a]	468
independent reflections	572
F (000)	208
number of parameters	43
largest diff peak (e$^-$/Å^3)	0.73
R[b], R_w[c] (%)	3.2, 3.7

[a] $F_o > 3s(F_o)$

[b] $R = S(|F_o| - |F_c|)/S(|F_o|)$

[c] $R_w = [S(w(|F_o| - |F_c|)^2)/S(w|F_o|^2)]^{1/2}$, $w = s(F_o)^{-2}$

Table II. Positional Parameters for Ca_3VN_3

Atom	Site	x	y	z
V	2e	0.8028(2)	0.25	0.3028(2)
Ca(A)	2e	0.3915(2)	0.25	0.8915(2)
Ca(B)	2e	0.9021(2)	0.25	0.8297(2)
Ca(C)	2e	0.3298(2)	0.25	0.4022(2)
N(A)	2e	0.6268(9)	0.25	0.1271(9)
N(B)	2e	0.3180(10)	0.75	0.4315(9)
N(C)	2e	0.9317(10)	0.75	0.8159(9)

Table III. Important Distances (Å) and Angles (deg) in Ca_3VN_3

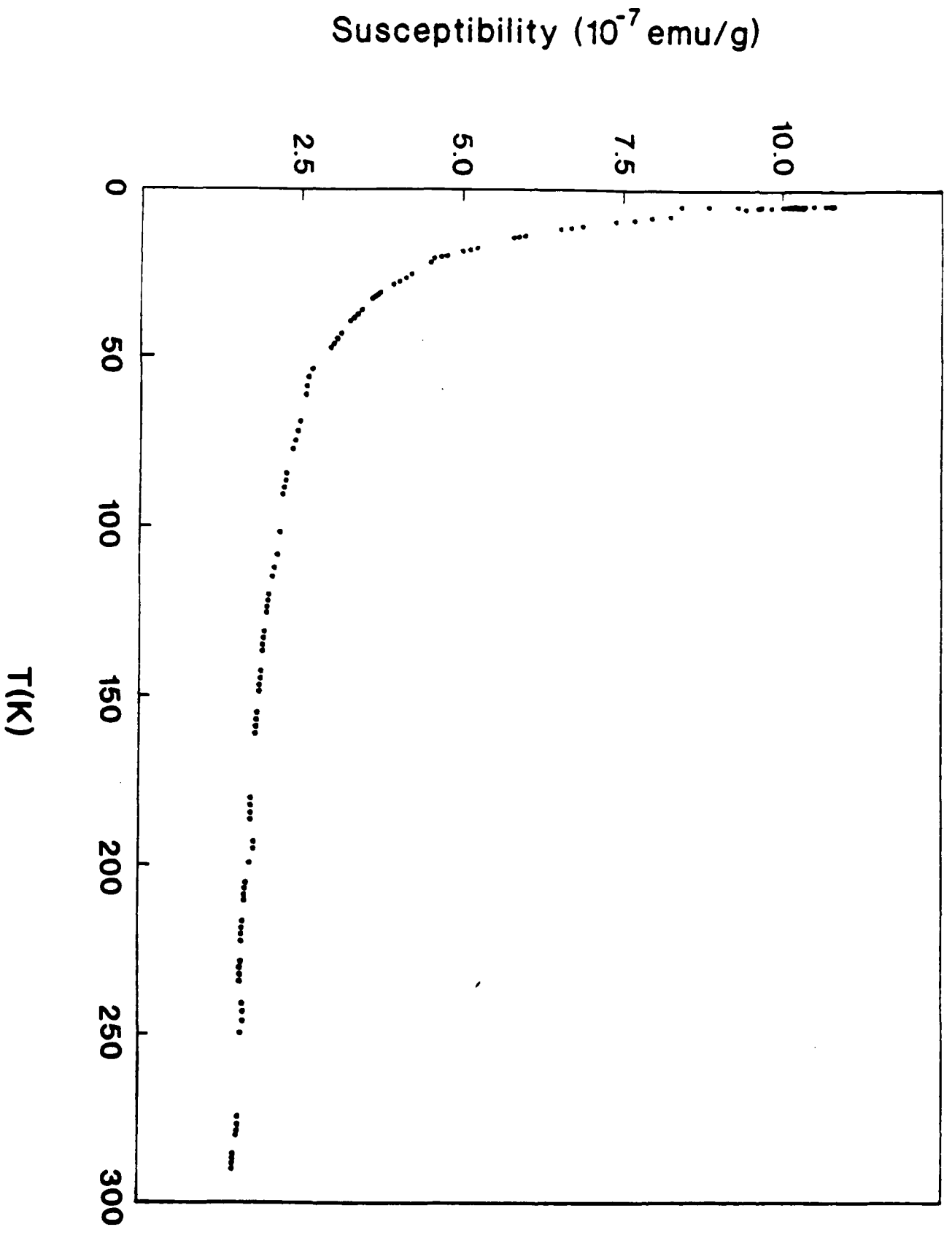
Bond Distances		Bond Angles	
V(1) - V(2)	5.086(2)	N(1C) - V(1) - N(1A)	114.8(3)
V(1) - V(3)	5.064(2)	N(1C) - V(1) - N(1B)	130.7(3)
V(1) - Ca(2C)	3.232(2)	N(1B) - V(1) - N(1B)	114.8(3)
V(1) - Ca(2A)	3.237(2)		
V(1) - Ca(2B)	3.233(2)		
V(1) - N(1B)	1.820(6)		
V(1) - N(1A)	1.827(7)		
V(1) - N(1C)	1.811(6)		
Ca(2A) - N(2B)	2.616(6)		
Ca(2A) - N(1A)	2.539(1)		
Ca(2A) - N(1A)	2.443(6)		
Ca(1C) - N(1A)	2.445(6)		

Figure Captions

Figure 1. Temperature dependence of the magnetic susceptibility of Ca_3VN_3.

Figure 2. A view of Ca_3VN_3 down the unique axis. The Ca atoms are dotted circles, the V atoms are open circles, and N atoms are completely hatched circles.

Figure 3. A view perpendicular to the unique axis shows the stacking arrangement and the labels used to identify atoms in Table III. Some atoms in the unit cell are not included for clarity.


Susceptibility (10^{-7} emu/g)
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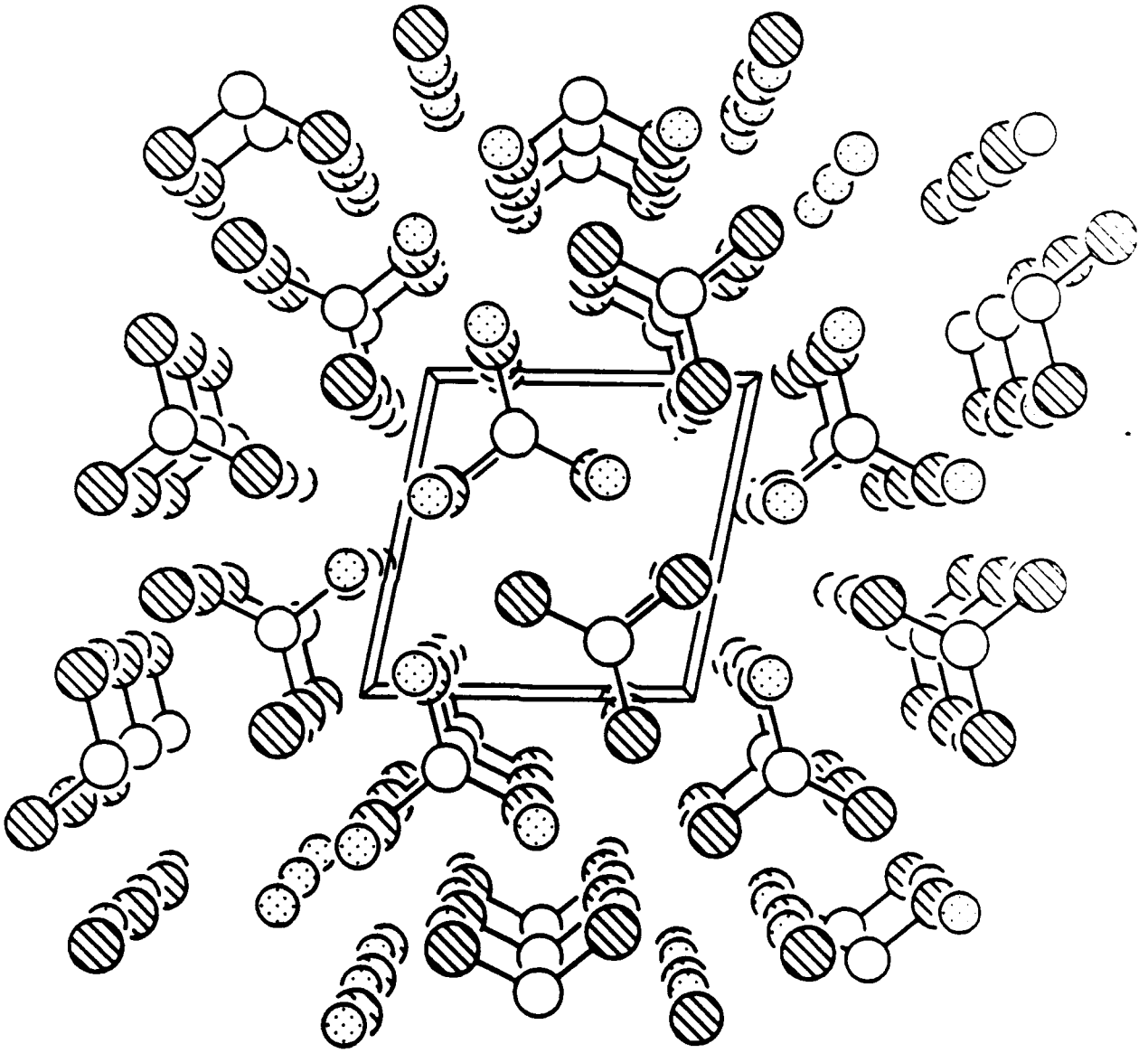
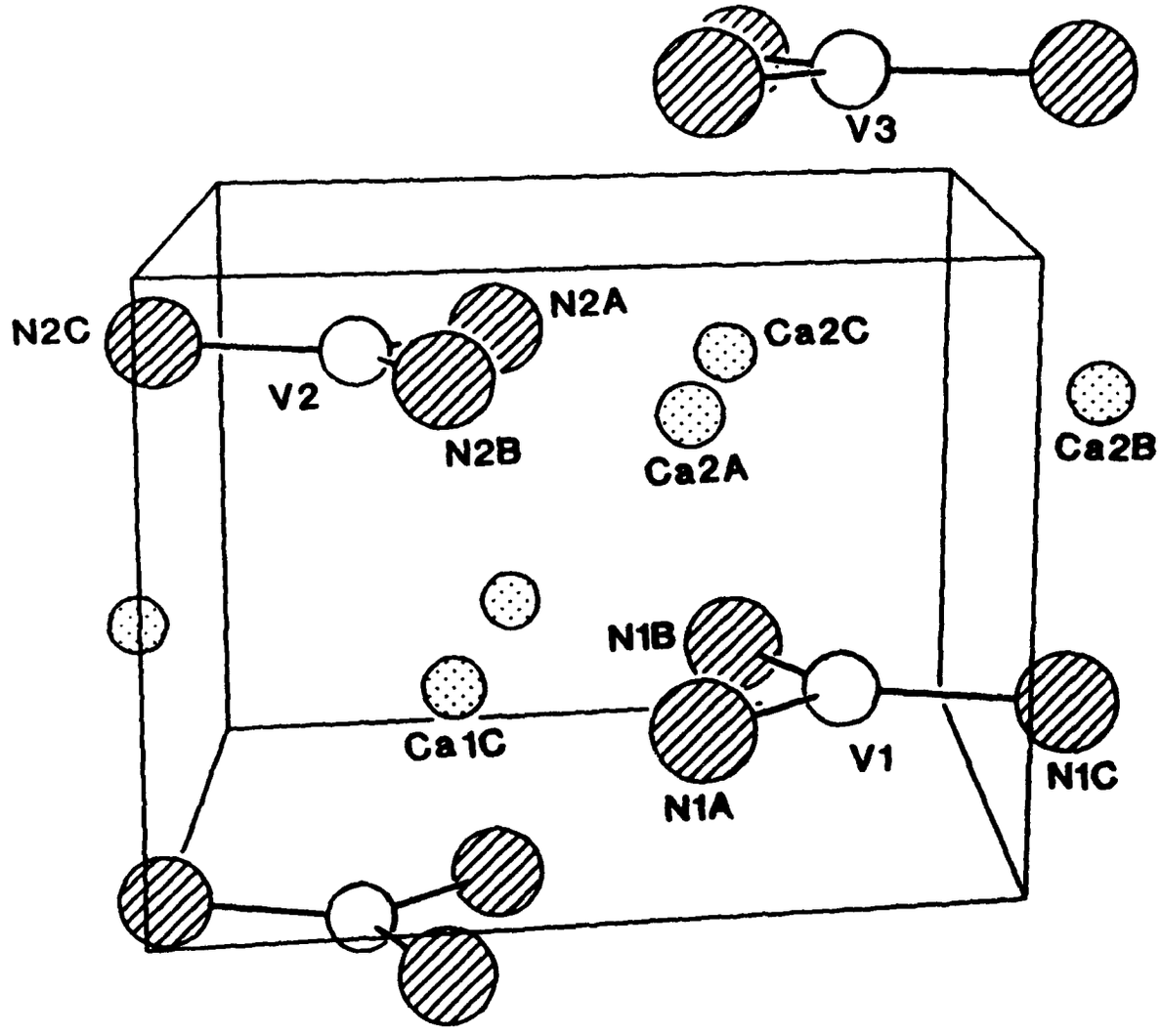
5.0
7.5
10.0
0
50
100
150
200
250
300
T(K)




V3
N2C
N2A
V2
N2B
Ca2C
Ca2A
Ca2B
N1B
Ca1C
V1
N1C
N1A

Supplementary Material

Observed and calculated structure factors for Ca_3VN_3

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
1	0	0	37	-49	5	0	0	1	40	47	7	7	3	1	166	-172	10	1	1	2	450	-440	27	0	5	2	394	405	22
2	0	0	304	-293	3	1	0	1	181	177	3	-6	4	1	462	-473	27	2	1	2	326	-324	3	1	5	2	224	-226	10
3	0	0	214	199	4	2	0	1	227	219	3	-5	4	1	91	82	8	3	1	2	17	5	-12	2	5	2	158	-155	8
4	0	0	480	-479	5	3	0	1	341	-338	3	-4	4	1	235	237	17	4	1	2	163	-152	4	3	5	2	46	14	-23
5	0	0	77	80	9	4	0	1	840	-856	7	-3	4	1	85	94	9	5	1	2	151	148	6	4	5	2	108	-109	8
6	0	0	22	2	-16	5	0	1	85	81	10	-2	4	1	277	285	22	6	1	2	125	-129	6	5	5	2	102	87	9
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7	1	0	32	-2	-13	-3	1	1	71	68	12	-5	5	1	75	-72	12	-1	2	2	443	451	40	-5	0	3	131	128	8
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2	5	0	391	402	11	7	2	1	25	-43	-25	1	0	2	229	-224	4	-5	4	2	108	114	15	5	1	3	368	363	5
3	5	0	80	-80	8	8	2	1	333	-334	22	2	0	2	1056	-1007	9	-4	4	2	82	-101	9	6	1	3	126	126	6
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0	6	0	571	-558	28	-5	3	1	103	98	13	5	0	2	347	-350	4	-1	4	2	287	-286	14	-7	2	3	271	-265	15
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2	6	0	105	103	6	-3	3	1	62	-56	-26	7	0	2	123	145	11	1	4	2	132	-125	5	-5	2	3	119	-117	7
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-8	0	1	24	46	-24	-1	3	1	27	0	-18	-7	1	2	97	-104	9	3	4	2	285	277	7	-3	2	3	392	404	25
-7	0	1	56	-24	-21	0	3	1	110	116	6	-6	1	2	87	88	9	4	4	2	75	71	10	-2	2	3	229	231	16
-6	0	1	646	-634	6	1	3	1	31	0	-17	-5	1	2	38	-15	-19	5	4	2	242	-232	8	-1	2	3	141	-134	5
-5	0	1	108	122	9	2	3	1	340	-333	18	-4	1	2	396	-398	17	6	4	2	123	118	8	0	2	3	163	153	5
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-3	0	1	183	158	4	4	3	1	87	-55	12	-2	1	2	28	-1	-15	-3	5	2	53	35	-18	2	2	3	408	395	18
-2	0	1	588	566	7	5	3	1	238	241	10	-1	1	2	324	332	25	-2	5	2	50	0	-22	3	2	3	155	-149	4
-1	0	1	75	-71	6	6	3	1	401	402	22	0	1	2	790	781	48	-1	5	2	183	183	9	4	2	3	164	-160	10

Observed and calculated structure factors for Ca_3VN_3

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
5	2	3	336	-334	4	6	0	4	166	166	8	-3	5	4	202	200	18	3	3	5	309	-308	22	-1	3	6	106	107	8
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7	2	3	341	331	6	8	0	4	284	-279	7	-1	5	4	311	-310	10	5	3	5	150	-148	10	1	3	6	419	-420	31
8	2	3	27	-10	-19	-6	1	4	67	-61	14	0	5	4	123	-123	10	6	3	5	25	-13	-17	2	3	6	115	109	8
-6	3	3	325	324	17	-5	1	4	78	68	15	1	5	4	53	-43	-24	-3	4	5	98	95	10	3	3	6	101	105	9
-5	3	3	191	-194	7	-4	1	4	22	2	-15	2	5	4	103	-112	8	-2	4	5	110	-114	8	4	3	6	154	-161	16
-4	3	3	259	-259	14	-3	1	4	317	320	7	3	5	4	242	235	13	-1	4	5	88	85	10	5	3	6	24	10	-17
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-2	3	3	58	-34	14	-1	1	4	523	-515	23	-6	0	5	128	127	11	1	4	5	82	63	13	-2	4	6	25	10	-18
-1	3	3	64	58	12	0	1	4	224	-227	6	-5	0	5	507	-507	5	2	4	5	243	240	10	-1	4	6	490	495	29
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2	3	3	30	14	-18	3	1	4	395	390	9	-2	0	5	141	-155	8	5	4	5	360	-359	11	2	4	6	118	119	11
3	3	3	339	333	10	4	1	4	95	-92	7	-1	0	5	115	127	9	-1	5	5	69	72	16	3	4	6	283	-290	15
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7	3	3	114	-104	10	8	1	4	136	138	9	3	0	5	369	379	4	3	5	5	243	235	17	-1	0	7	23	-25	-23
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-3	4	3	296	-298	20	-4	2	4	214	-208	11	6	0	5	25	-42	-25	-3	0	6	206	-195	6	2	0	7	153	-160	8
-2	4	3	156	-164	15	-3	2	4	350	349	12	7	0	5	26	-34	-26	-2	0	6	23	18	-23	3	0	7	373	-376	5
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-3	5	3	24	1	-17	7	2	4	73	-98	24	3	1	5	380	372	3	-4	1	6	53	62	-21	3	1	7	126	125	20
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-1	5	3	53	-41	-23	-4	3	4	22	-2	-16	5	1	5	167	170	5	-2	1	6	99	-87	12	5	1	7	359	-378	4
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4	5	3	245	-236	14	1	3	4	88	58	14	-3	2	5	120	-119	7	3	1	6	135	-127	6	0	2	7	274	-270	16
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-1	6	3	83	-82	17	3	3	4	323	-315	17	-1	2	5	110	-112	9	5	1	6	23	-7	-16	2	2	7	143	148	21
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-3	0	4	383	-388	4	-2	4	4	102	-104	8	6	2	5	24	38	-17	0	2	6	26	-6	-19	1	3	7	193	-186	10
-2	0	4	157	-158	6	-1	4	4	242	-242	20	7	2	5	34	33	-20	1	2	6	22	25	-16	2	3	7	145	-133	8
-1	0	4	388	-381	5	0	4	4	287	-301	15	-4	3	5	70	-65	15	2	2	6	142	-145	14	3	3	7	114	-109	8
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3	0	4	171	-178	5	4	4	4	274	283	15	0	3	5	85	84	13	6	2	6	384	385	5	1	0	8	368	-384	5
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5	0	4	41	-72	-41	6	4	4	127	124	14	2	3	5	127	124	21	-2	3	6	87	82	10	3	0	8	24	-15	-24

Observed and calculated structure factors for Ca_3VN_3

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
4	0	8	289	-286	6	0	1	8	184	-189	8	3	1	8	147	-149	7	0	2	8	122	124	8	2	2	8	220	-226	10
5	0	8	160	160	9	1	1	8	75	-65	14	4	1	8	129	138	12	1	2	8	365	362	14	3	2	8	29	14	-21
-1	1	8	393	400	5	2	1	8	96	84	18																		

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