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Synthesis, Structure, Electric, and Magnetic Properties of CaNiN

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We report the synthesis and physical properties of the new ternary nitride CaNiN, prepared by the reaction of Ca_3N_2 and Ni in N_2 gas at 1000°C. The structure, determined by the method of X-ray powder diffraction, is tetragonal ($P4_2/mmc$) with a = 3.5809(2) Å, c = 7.0096(3) Å, and Z = 2. While the structure is a simple but uncommone one, with all atoms occupying fixed special positions, it features interesting —Ni–N–Ni–N— linear chains. Conductivity and magnetic measurements show that CaNiN is metallic and paramagnetic.

Introduction

There are only few known ternary nitrides containing both transition and alkaline earth metals (*1–3*). Our recent research in nitrides has focused on the synthesis of ternary phases containing calcium and a transition metal; at least one new ternary compound is found in each Ca–*M*–*N* system. As part of this investigation, we report here the synthesis and properties of a new compound, CaNiN.

The oxidation state of Ni(I) in CaNiN is quite unusual for a solid state compound. Formally Ni(I) exists in hexagonal Ni_3N (*4, 5*). But the structure of Ni_3N is basically a tripled face-centered cubic nickel framework with "interstitial" nitrogen in the octahedral holes, and has extensive Ni–Ni bonding. Another similar example is Ni_3S_2 (*6*), in which formally Ni(I) and Ni(II) occur, but short Ni–Ni distances comparable with that in metallic nickel are again indicative of metal–metal bonding (*7*). In CaNiN, the Ni–Ni distance is far too long to have any Ni–Ni interaction. A complete description of this unusual phase follows.

Sample Preparation

CaNiN was prepared by heating in an alumina crucible a pressed pellet of Ca_3N_2 and fine nickel powder in an N_2 atmosphere at 1000°C for 2 days. N_2 gas (99.995%) was further purified by passing it through a column of finely divided copper powder at 150°C and then a column of activated molecular sieves to remove traces of O_2 and H_2O. Since at 1000°C Ca_3N_2 will slowly sublime, and since it is very sensitive to even minute amounts of O_2 and H_2O remaining in the N_2 gas to produce CaO, we further protected the sample by sandwiching it with two boats of fine calcium nitride powder, and we also added a 10% excess Ca_3N_2 to compensate for the calcium loss from sublimation and oxide formation. The approximate stoichiometry of the ternary compound was estimated in the following way. A pellet of Ca_3N_2 of similar size was simultaneously

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TABLE I

X-RAY POWDER DIFFRACTION DATA ($\lambda_{\mathrm{Cu}K\alpha_1}$ = 1.540560 Å) FOR CaNiN

hkl	d_{obs} (Å)	d_{calc} (Å)	$I/I_{0,\mathrm{obs}}$	$I/I_{0,\mathrm{calc}}$
100	3.0928	3.0928	3	2
002	3.5050	3.5048	6	5
101	3.1884	3.1889	5	4
[a]	2.7818		1	
110	2.5320	2.5321	38	39
102	2.5048	2.5047	100	100
[a]	2.4117		3	
112	—	2.0525	<1	<1
103	1.9568	1.9568	1	1
200	1.7902	1.7905	20	21
004	1.7525	1.7524	10	10
201	—	1.7348	<1	<1
[a]	1.7064		1	
210	—	1.6014	—	0
202	1.5942	1.5944	1	1
104	—	1.5740	<1	<1
211	—	1.5612	<1	<1
212	1.4566	1.4566	29	32
114	1.4409	1.4410	11	12
203	—	1.4212	—	0
213	—	1.3210	<1	<1
105	—	1.3054	<1	<1
220	1.2660	1.2661	5	6
204	1.2524	1.2524	10	11
300	—	1.1936	<1	<1
222	—	1.1907	<1	<1
214	—	1.1822	<1	<1
301	—	1.1767	<1	<1
006	—	1.1683	<1	<1
310	1.1327	1.1324	4	5
302	1.1302	1.1299	6	7
311	—	1.1179	—	0
106	1.1103	1.1106	6	6
205	—	1.1038	—	0
312	—	1.0775	<1	<1
303	—	1.0630	<1	<1
116	—	1.0608	<1	<1
215	—	1.0548	<1	<1
224	1.0261	1.0262	6	6
313	—	1.0190	—	0
320	—	0.9932	<1	<1
304	—	0.9865	<1	<1
321	—	0.9834	<1	<1
206	—	0.9784	<1	<1
107	—	0.9644	<1	<1
322	0.9556	0.9556	7	9
314	0.9511	0.9512	4	7

[a] Impurity lines due to CaO.

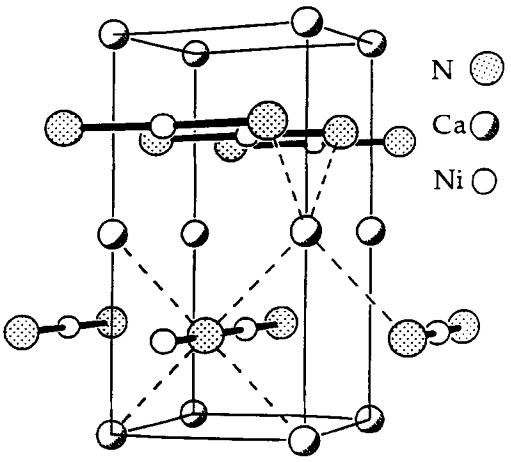

FIG. 1. Crystal structure of CaNiN. The unit cell is drawn by the full lines. The nickel and the nitrogen atoms are connected by the bold lines. The dashed lines connecting Ca–N and Ca–Ni show that calcium is tetrahedrally coordinated by nitrogen, and that nitrogen is in the octahedral hole surrounded by two nickel and four calcium atoms.

heated adjacent to the ternary phase. The weight loss from sublimation of the Ca_3N_2 pellet was found to be typically 7%. The amount of second phase, identified as CaO, in the Ca–Ni–N system estimated by X-ray diffraction was about 3%. The final weight of the ternary compound then indicates a composition CaNiN. The density of the sample was measured by a simple density apparatus (*8*).

Since nitrogen is a light element, the nitrogen stoichiometry cannot be accurately determined by the weight gain or density alone. To measure the nitrogen content, a modified Dumas method (*9*) was used. The sample was ground to a fine powder and was heated in a furnace in a CO_2 flow. Approximately at 700°C the sample starts to react with CO_2 to produce CO, N_2, $CaCO_3$, and Ni. The reaction was complete in 5 min at 1000°C. The CO was converted back to CO_2 by reaction with I_2O_5. The N_2 and CO_2 were then passed through a concentrated KOH solution; the CO_2 was absorbed and the volume of the N_2 measured. The nitrogen content determined this way gives a stoichiometry $CaNiN_{0.98\pm1\%}$.

In our first synthesis reactions, we used a −400 mesh nickel powder, but a significant percentage of unreacted nickel remained even after several regrinding and reheating cycles. This made the magnetic susceptibility measurement difficult, because small amounts of ferromagnetic nickel can overwhelm the susceptibility of most materials. When submicron size nickel powder (Aldrich, 99.8%) was used, we could not detect free nickel either by X-ray diffraction or by a magnet after the first firing. This fact indicates that the diffusion rate for the calcium or nickel in the solid is quite low at 1000°C.

CaNiN is a black powder and decomposes after several hours of exposure to moist air to produce NH_3.

Crystal Structure

X-ray intensity data were taken on a powder sample with a Scintag XDS 2000 diffractometer using (Cu$K\alpha$ radiation. The (Cu$K\alpha_2$ lines were stripped using the Scintag software. Data were collected over a 2θ range 5–110 degrees. The sample was loaded in an aluminum holder and covered with a 0.5-mil-thick layer of Mylar in a dry box to avoid air exposure. The mylar sheet was supported by two semicircular disks standing perpendicularly to the sample so that the absorption due to the mylar is uniform and small over the whole 2θ range.

The diffraction peaks were sharp and the pattern was indexed on a tetragonal unit cell by trial and error (a = 3.5809(2) Å, c = 7.0096(3) Å). The systematic absences ($l = 2n$ for both hhl and $00l$) suggest three possible tetragonal space groups: $P4_2mc$, $P\bar{4}2c$, and $P4_2/mmc$. Because the X-ray pattern has the additional feature that all the strong lines correspond to the condition either $h + k + l = 2n$ or $hk(l = 2n)$, we chose the space group of highest number, $P4_2/mmc$ (No. 131), and located the atoms at special positions which satisfy this observation and produce reasonable bond lengths, i.e., Ca at (2e) 0,0,1/4; 0,0,3/4, Ni at (2b) 1/2,1/2,0; 1/2,1/2,1/2, and N at (2c) 0,1/2,0; 1/2,0,1/2. The calculated intensities obtained by the program Lazy (*10*) show an excellent agreement with the measured integrated intensities (see Table I). The theoretical density derived from the above structureis 4.17 g/cm^3, which agrees very well with the measured density of 4.13 g/cm^3.

TABLE II

INTERATOMIC DISTANCES FOR CaNiN

Ni–Ni[a]	3.5809 Å	Ni–Ni[b]	3.5048 Å
Ni–N	1.7904 Å	Ca–N	2.5053 Å
Ni–Ca	3.0352 Å		

[a] Distance between parallel chains.

[b] Distance between perpendicular chains.

The unit cell, which contains two formula units, is shown in Fig. 1 (we have shifted the origin by 0,0,1/4 for a clearer view.) In the structure, nickel is coordinated linearly to nitrogen to form chains of —Ni–N–Ni–N—. The chains are stacked in a way that there are layers of parallel chains, but chains in adjacent layers run in perpendicular directions. Calcium occupies the tetrahedral holes between the layers, and nitrogen is in approximately octahedral coordination with two nickel and four calcium near-neighbor atoms. The interatomic distances are summarized in Table II.

Conductivity Measurement

Four-probe conductivity measurements were performed on sintered pellets at 13 Hz by lock-in detection. The sample dimensions were 1/2 in. in diameter and 50 mil in thickness. Four spring-loaded pins arranged in a collinear configuration were pressed against the pellet to serve as the contacts, which were shown to be ohmic from the

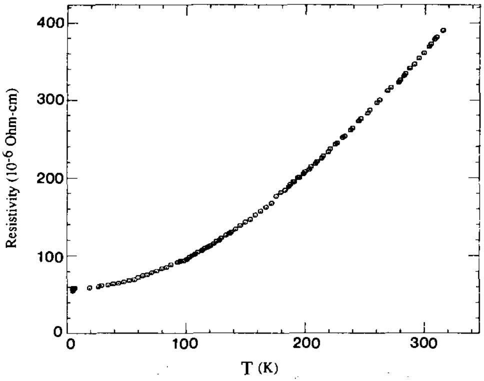

FIG. 2. Temperature dependence of the resistivity of CaNiN.

linearity of the I–V characteristic. To prevent air exposure, the moisture-sensitive sample was covered in a glove box by a lucite cap which also supports the four spring-loaded pins. We calibrated the system by measuring the resistance of a piece of solid molybdenum of the same thickness and diameter as the nitride sample, and a proportionality constant between the resistivity and the resistance of the Mo was obtained (*11*). This value was then used to convert the resistance to the resistivity for CaNiN. This conversion assumes that we are measuring the isotropic conductivity of a randomly oriented polycrystalline sample. The temperature dependence of the resistivity from 4 to 320 K is shown in Fig. 2. The magnitude of the resistivity and the decrease with the decreasing temperature indicate simple metallic behavior typical of a transition metal compound.

Magnetic Susceptibility Measurement

The Faraday technique was used to measure the magnetic susceptibility of the sample. The susceptibility was measured as a function of the applied field, and it was found to be field dependent, indicating a small contamination by ferromagnetic impurities. The contribution of this ferromagnetic impurity was substracted from the data by the method of Owen and Honda (*12*). Assuming that this is due to a very small amount of unreacted nickel, we estimate from the magnitude of this correction that the weight fraction of the unreacted Ni was about 0.05% (10^{-4} g). The ferromagnetic moment was measured at several different temperatures: 20 K, 100 K, 200 K, and 300 K. The moment had a larger temperature dependence than that of bulk nickel (the percentage change between 20 K and 300 K was four times as large as for bulk nickel). This may be due to a very small particle size of ferromagnetic impurity. Figure 3 shows the susceptibility corrected for the ferromagnetic impurity from 4 to 320 K. It is apparent that a temperature-dependent paramagnetism remains. This paramagnetism is approximately proportional to $1/T$ at high temperatures and saturates near 7 K (Fig. 4), indicating an antiferromagnetic ordering. Assuming that each Ni has $s = 1/2$ and $g = 2$, we find that only 5% of the Ni would have a magnetic moment by fitting the data with the Curie–Weiss law at high temperatures. There are two possibilities for the origin of this small paramagnetic contribution: it is

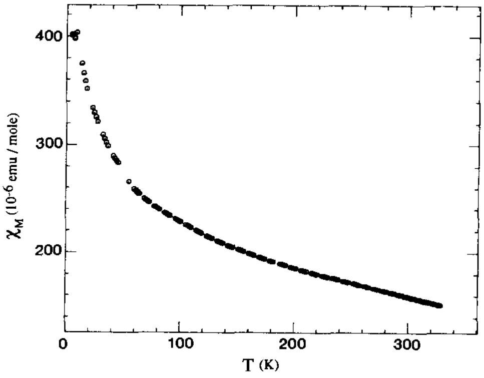

FIG. 3. Temperature dependence of the magnetic susceptibility of CaNiN, after a small contribution from the ferromagnetic impurity has been subtracted.

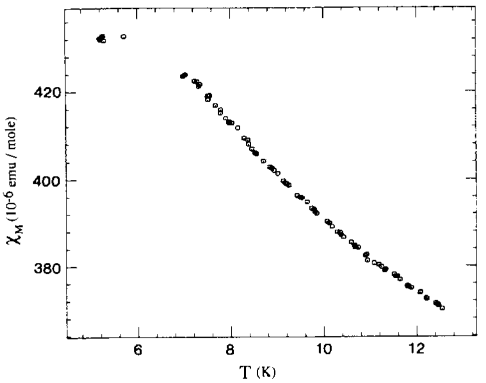

FIG. 4. The susceptibility of the sample is observed to saturate below 7 K.

intrinsic to the material so that each Ni has a small moment of 0.39 μ_B, or it is due to a small amount of paramagnetic impurities in the CaNiN. If the impurity were Fe with a moment of 5.9 μ_B, then about 0.5% Fe would be required, but this seems a little high. Only microscopic measurements can determine the origin of this moment unambiguously. Finally, a constant paramagnetic susceptibility is obtained when the data are extrapolated to infinite temperature. This susceptibility is obtained when the data are extrapolated to infinite temperature. This susceptibility is assumed to be intrinsic to the sample and has the value (64 ± 10) × 10^{-6} emu/mole.

Discussion

In CaNiN, the shortest Ni–Ni distance of 3.50 Å is much longer than the Ni–Ni distance of 2.49 Å in nickel metal, indicating very weak Ni–Ni interactions. However, the Ni–N distance, 1.79 Å, is shorter than the Ca–N distance, 2.51 Å; substantial bonding between the nickel and the nitrogen in CaNiN is obvious. In the solid–solution $Li_{3-x}Ni_xN$ ($x < 0.6$) the nickel replaces some of those lithium atoms bonded to two nitrogen atoms in Li_3N (*13*). The nickel in that phase is therefore also linearly coordinated to two nitrogen atoms. The Ni–N distance in CaNiN is within the range of variation of the Ni–N bond length of that compound, from 1.91 to 1.76 Å as x goes from 0.1 to 0.6 The Ca–N distance, 2.51 Å, in CaNiN is close to the average value, 2.47 Å, in Ca_3N_2 (*14*). The Ca–Ni distances in the intermetallic compounds $CaNi_2$ and $CaNi_5$ are 3.01 and 3.00 Å, respectively (*15*), which are also close to the Ca–Ni distance of 3.04 Å in this nitride.

Two interesting features of this compound are the octahedrally coordinated nitrogen and the —Ni–N–Ni–N— linear chains. In the ternary calcium nitrides so far examined, the nitrogen is coordinated by six metal atoms that form a (distorted) octahedron about the nitrogen. Examples are the anti-perovskite Ca_3XN (X = Bi, Sb, As, P, Pb, Sn, Ge) (*16*), Ca_2ZnN_2 (*17*), $Ca_{1-x}Ti_xN$ (*18*), the intermetallic compound Ca_4In_2N (*19*), and CaGaN (*20*). Quasi-one-dimensional compounds often exhibit interesting physical properties such as charge density waves or a Peierls distortion (*21*). But we did not observe any anomaly in either the conductivity or the magnetic susceptibility from 4 to 320 K.

Although this compound has a simple structure with atoms in special positions, it is uncommon. The same structure type has been found only in YCoC (*22*) and SrLiN (*23*). The band structure of YCoC has been previously reported (*24*). Without any significant change we can apply the band structure for YCoC to CaNiN (*25*). Assuming that calcium is so electropositive that it is taken as 2^+, the total number of electrons per $(NiN)^{2-}$ unit is 17. We take the direction of the chain as the z direction. The p_z orbital of nitrogen interacts with the d_{z^2} orbital of nickel to form bonding σ and anti-bonding σ^* bands. The p_x and p_y orbitals of nitrogen have π interactions with the d_{xz} and d_{yz} orbitals of nickel, respectively; the d_{xy} and $d_{x^2-y^2}$ orbitals of nickel do not participate in bonding. The σ^* band has the highest energy, the π^*, d_{xy}, $d_{x^2-y^2}$, π, and bands reside in the middle, and the σ band has the lowest energy. The 17 electrons then fill these 8 bands and a lower band derived from the nitrogen *s* orbital. Since the bands can accommodate 18 electrons, the Fermi level lies in a partially filled σ^* band, and CaNiN is thus expected to be metallic as observed. However, these bands are very one-dimensional because the dispersion perpendicular to the chain direction is very small (0.2 eV perpendicular to chain compared to 1.5 eV along the chain for the conduction band). The lack of a Peierls distortion is therefore puzzling.

Summary

We have observed metallic behavior in CaNiN. Due to small amounts of paramagnetic impurity, we obtain only an approximate value for the temperature-independent paramagnetic susceptibility of CaNiN. The origin of the temperature-dependent susceptibility is uncertain, but is likely due to an impurity at the 0.5% level. It would be interesting to grow single crystals to explore the anisotropy in properties and for more accurate measurements. In CaNiN the oxidation state of the nickel is 1^+, and the electronic configuration for Ni (I) is d^9. In high-temperature superconductors copper has a d^9 configuration. One of our current efforts is to further study the nickel nitride chemistry to see if analogues of the copper oxides can be obtained.

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References

1. F. K. Patterson and R. Ward, *Inorg. Chem.* **5,** 1312 (1966).
2. R. Karam and R. Ward, *Inorg. Chem.* **9,** 1849 (1970).
3. J. P. Motte and R. Streiff, *Compt. Rend. C* **267,** 1598 (1968).
4. R. Juza and W. Sachsze, *Z. Anorg. Allg. Chem.* **251,** 201 (1943).
5. K. H. Jack, *Acta Crystallogr.* **3,** 392 (1950).
6. A. Westgren, *Z. Anorg. Allg. Chem.* **239,** 82 (1938).
7. J. B. Parise, *Acta Crystallogr. Sect. B* **36,** 1179 (1980).
8. To be published.
9. G. M. Gustin and C. L. Ogg, *in* "Treatise on Analytical Chemistry," Part II, "Analytical Chemistry of Inorganic and Organic Compounds" (I. M. Kolthoff and P. J. Elving, Eds.), Vol. 11, p. 405. Wiley-Interscience, New York (1965).
10. K. Yvon, W. Jeitschko, and E. Parthé, *J. Appl. Crystallogr.* **10,** 73 (1977).
11. J. D. Wasscher, *Philips Res. Rep.* **16,** 301 (1961).
12. P. W. Selwood, "Magnetochemistry," p. 186, Wiley-Interscience, New York (1979).
13. V. W. Sachsze and R. Juza, *Z. Anorg. Allg. Chem.* **259,** 278 (1949).
14. Y. Laurent, J. Lang, and M. T. LeBihan, *Acta Crystallogr. Sert. B* **24,** 494 (1968).
15. "Pearson's Handbook of Crystallographic Data for Intermetallic Phases" (P. Villars and L. D. Calvert, Eds.), Amer. Soc. Metals, Metals Park, OH (1985).
16. To be published.
17. To be published
18. To be published
19. G. Cordeied and S. Rönniger, *Z. Naturforsch. B* **42,** 825 (1987).
20. P. P. Verdier, P. L'Haridon, and M. Marchand, *Acta Crystallogr., Sect. B* **30,** 226 (1974).
21. F. J. DiSalvo and T. M. Rice, *Phys. Today* **32**(4), 32 (1979).
22. M. H. Gerss and W. Jeitschko, *Z. Naturforsch., B* **41,** 946 (1989).
23. G. Cordier, A. Gudat, R. Kniep, and A. Rabenau, *Angew. Chem. Int. Ed. Engl.* **2,** 28 (1989).
24. R. Hoffmann, J. Li, and R. A. Wheeler, *J. Amer. Chem. Soc.* **109,** 6600 (1987).
25. J. Li, private communication.