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Intermetallic Frameworks: Synthesis, Characterization, and Bonding of $K_{0.4}Cd_2$ and $Na_{26}Cd_{141}$

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Two new compounds have been synthesized and characterized in the systems A−Cd where A = Na or K. They have identical ratios of alkali-metal to cadmium but have remarkably different structures. The potassium compound, $K_{0.368(9)}Cd_2$ (tetragonal, *I*4/*mcm*, $a = 9.169(1)$, $c = 2.8779(5)$ Å, $Z = 2$), has a zeolite-like frame built of cadmium, and with channels that are fractionally occupied by potassium. The sodium counterpart, $Na_{26}Cd_{141}$ (hexagonal, *P*6/*mmm*, $a = 21.306(3)$, $b = 9.625(2)$ Å, $Z = 1$) is with the same alkali-metal fraction, $Na_{0.369}Cd_2$, but with a three-dimensional alloy-like structure. With the exception of one atom, it is isostructural with $Y_{26}Pd_{80}Sn_{62}$. Structurally it differs substantially from the known Na_2Cd_{11} ($Na_{26}Cd_{143}$) although the stoichiometries are very similar. Magnetic measurements and results from electronic structure calculations are reported as well.

Introduction

A great number of solid-state compounds containing isolated clusters and/or networks of clusters of the boron group has been discovered in the past few years.[1] This large variety warrants studies on possible isoelectronic substitutions of the boron group element by mixtures of elements from other groups in order to form isoelectronic heteroatomic clusters. For example, a known compound A_xE_y where A is an alkali-metal and E is a boron group element, is replaced by the isoelectronic compound $A_xE'_{y/2}E''_{y/2}$ where E′ and E″ represent elements of groups 12 and 14, respectively. Often the structural preferences of an element in a compound depend solely on the number of available electrons.[2] We have been interested in testing this principle rather on mixtures of elements and explore for new cluster compounds. This strategy has resulted in two novel structures with heteroatomic clusters of Cd/Sn and Cd/Pb.[3] The first large clusters of the carbon group in neat solids were discovered as side products of such syntheses as well.[4] Here we report on two compounds, $K_{0.4}Cd_2$ and $Na_{26}Cd_{141}$, found also as byproducts of the studied heteroatomic systems. Structurally the first one can be considered an intermetallic analogue of the microporous zeolites, aluminophosphates, and other oxides with open-framework structures. The framework is built of cadmium and is “stuffed” with the alkali metal.

Experimental Section

Syntheses. Both $K_{0.4}Cd_2$ (exact stoichiometry $K_{0.368(9)}Cd_2$) and $Na_{26}Cd_{141}$ are air sensitive, and all operations were performed under inert atmosphere or vacuum. Details on the handling can be found elsewhere.[3] The potassium compound was initially identified in the product of reaction loaded as $K_8Cd_5Sn_5Zn$ (isoelectronic with the known $K_8In_{10}Zn$[5]), heated at 650 °C for 2 days, and cooled to room temperature at a rate of 5°/h. After the structure of the compound was determined it was clear that zinc was not included, but the Cd:Sn ratio was ambiguous due to the proximity of the two elements in the periodic table. Scanning electron microscopy combined with energy dispersive microprobe analysis of two crystals revealed the presence of K and Cd only. The compound was later synthesized in 100% yield (based on a Guinier powder pattern) from a stoichiometric mixture of K and Cd (both from Alfa-Aesar). The mixture was heated at 600 °C for 12 h and then quenched in liquid nitrogen. The phase width of $K_{0.4}Cd_2$ seems to be relatively narrow since the lattice parameters change only within 6σ for the products of reactions loaded with K:Cd ratios in the range of 1:1 to 1:8. The structure was also found in quenched samples of K−Na−Cd.

$Na_{26}Cd_{141}$ (loaded as $Na_{0.4}Cd_2$) was made in an attempt to synthesize the sodium analogue of $K_{0.4}Cd_2$. The mixture of Na (Alfa-Aesar) and Cd was treated in the same way as for $K_{0.4}Cd_2$. Similar cesium and rubidium compounds seem to be nonexistent.

X-ray Diffraction Studies. X-ray powder diffraction patterns of the reaction products were taken with Cu Kα_1 radiation on an Enraf-Nonius Guinier camera. The patterns were used to identify phases, and to obtain lattice parameters by least-squares refinement of the positions of the lines calibrated by an internal silicon standard (NIST).

Single-crystal diffraction data were collected from crystals mounted in glass capillaries on a CAD-4 diffractometer with monochromated Mo Kα radiation at room temperature ($2\theta \leq 50°$, full sphere with $\omega-2\theta$ scans from a needle-like crystal of size 0.4 × 0.05 × 0.05 mm for $K_{0.4}Cd_2$, and an octant with ω scans from an irregular crystal of size 0.08 × 0.16 × 0.18 mm for $Na_{26}Cd_{141}$). The structures were solved and refined with the aid of the SHELXTL-V5.0 software package. Details on the data collection and refinement are listed in Table 1. The final positional and equivalent isotropic displacement parameters and important distances for the refined structures are listed in Tables 2 and 3, respectively.

Structure Determinations. Oscillation and Weissenberg photos taken on crystals of $K_{0.4}Cd_2$ were consistent with three possible space groups: *I*4*cm*, *I*$\bar{4}$*c*2, and *I*4/*mcm*. Special attention was paid to possible superstructure along the very short *c* axis of the tetragonal cell, 2.8779

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Table 1. Crystal Data and Structure Refinement for $K_{0.368(9)}Cd_2$ and $Na_{26}Cd_{141}$

empirical formula	$K_{0.368(9)}Cd_2$	$Na_{26}Cd_{141}$
formula weight	239.21	16446.14
unit cell parameters:		
a, Å	9.169(1)	21.306(3)
c, Å	2.8779(5)	9.625(2)
V, Å^3	241.95(6)	3784(1)
space group, *Z*	*I*4/*mcm* (No. 140), 2	*P*6/*mmm* (No. 191), 1
density (calculated), g/cm^3	6.567	7.217
radiation, λ	Mo Kα, 0.710 73 Å	
temperature	293(2) K	
absorption coeff, cm^{-1}	177.67	193.82
R indices ($I > 2\sigma_I$)^a	R1 = 1.32%, wR2 = 3.13%	R1 = 2.99%, wR2 = 5.72%
R indices (all data)	R1 = 1.32%, wR2 = 3.13%	R1 = 4.68%, wR2 = 6.34%
secondary ext. coeff.	0.029(2)	0.000041(5)

^{a} R1 = $||F_o| - |F_c||/|F_o|$; wR2 = $[[w(F^2_o - F^2_c)^2]/[w(F^2_o)^2]]^{1/2}$; $w = 1/[\sigma^2F^2_o + (0.0176P)^2 + 0.5724P]$ for $K_{0.368(9)}Cd_2$; $w = 1/[\sigma^2F^2_o + (0.0188P)^2 + 10.2398P]$ for $Na_{26}Cd_{141}$; $P = (F^2_o + 2F^2_c)/3$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters

atom	*x*	*y*	*z*	*U*(eq)
		$K_{0.368(9)}Cd_2$		
Cd	0.14741(3)	0.35259(3)	1/2	0.0208(4)
K^a	0	0	0	0.16(4)
		$Na_{26}Cd_{141}$		
Cd(1)	0.60633(8)	0.60633(8)	0	0.0224(4)
Cd(2)	0.55370(4)	0.44630(4)	0	0.0182(4)
Cd(3)	0.31683(7)	0.23299(7)	0	0.0251(3)
Cd(4)	0.15021(9)	0.15021(9)	0	0.0272(4)
Cd(5)	0.52352(6)	0.26176(3)	0.3455(1)	0.0171(2)
Cd(6)	0.35816(6)	0.17908(3)	0.7564(1)	0.0176(3)
Cd(7)	0.61929(3)	0.38071(3)	0.1614(1)	0.0199(3)
Cd(8)	0.45432(5)	0.11074(4)	0.22425(7)	0.0229(2)
Cd(9)	0.18877(8)	0.09439(4)	0.2373(1)	0.0355(3)
Cd(10)	1/2	0	0.2459(2)	0.0197(4)
Cd(11)	0.40832(6)	0.12939(6)	1/2	0.0158(2)
Cd(12)	0.27306(9)	0.13653(4)	1/2	0.0155(3)
Cd(13)	0.13729(9)	0.13729(9)	1/2	0.0315(4)
Cd(14)	0.42041(8)	0	1/2	0.0197(4)
Cd(15)	1/3	2/3	1/2	0.0332(8)
Cd(16)	0	0	1/2	0.039(1)
Na(1)	0.2416(2)	0.4831(5)	0	0.026(2)
Na(2)	0.2766(3)	0	0.3086(6)	0.029(2)
Na(3)	0.1509(5)	0.5755(2)	1/2	0.024(2)
Na(4)	0	0	0.176(2)	0.055(6)

^{a} Refined with 36.7(9)% occupancy.

Å, but none was observed. Systematic extinctions in the CAD4 data confirmed the space group choices. The structure was solved in the centrosymmetric group, and the direct methods provided two positions. The refinement of the structure with both sites, one for cadmium and one for potassium, fully occupied resulted in unreasonable anisotropic displacement parameters for potassium. Also, the K−K distances between the equivalent positions were unreasonably short. This clearly suggested fractional occupancy of that site. Thus, the occupancy of the potassium was freed to vary, and the stoichiometry of the compound was refined as $K_{0.368(9)}Cd_2$ with final R1 and wR2 = 1.32 and 3.13%, respectively.

The data for $Na_{26}Cd_{141}$ were corrected for absorption with the aid of the average of three ψ scans, and the structure was solved in the centrosymmetric *P*6/*mmm* space group. Direct methods provided 16 cadmium positions. The four sodium positions were later identified from difference Fourier maps. Varying the occupancies of either the cadmium or the sodium sites while keeping fixed the remaining ones did not lead to deviations of more than 1σ, and all sites were kept fully occupied for the final refinement.

Magnetic Measurements. The magnetizations of 42 mg of $K_{0.4}Cd_2$ and of 52 mg of $Na_{26}Cd_{141}$ were measured at a field of 3 T over a temperature range of 10−295 K on a Quantum Design MPMS SQUID magnetometer.[3]

Results and Discussion

Structure Descriptions. The structure of $K_{0.4}Cd_2$ is best described as a framework of cadmium with one-dimensional voids occupied by the potassium cations (Figure 1). The construction resembles remarkably the structures of the zeolites where aluminosilicate frameworks have channels occupied by alkali-metal cations. The shortest Cd−Cd distance across the channel in $K_{0.4}Cd_2$ is more than 7 Å, and this dimension is comparable with the channels of the small-pore zeolites. Each cadmium atom is surrounded by 8 other atoms of the same kind. The latter form a bicapped trigonal prism (Figure 2a) where capped are the trigonal bases. The shortest and hence strongest bonding interactions between cadmium atoms are along the *c* axis, 2.8779(5) Å. The channels in $K_{0.4}Cd_2$ are made of staggered squares of cadmium stacked along the *c* axis. The potassium cations occupy the central line of the so formed "octagonal" channels. Surprisingly they are at the levels of the squares rather than being between them. (There are no Cd−Cd bonds within the squares since the distances are 4.955 Å.) Thus the coordination polyhedron around the potassium is a tetracapped square prism (Figure 2b) formed of two fused square antiprisms, and hence with four short and eight long K−Cd distances. The distances between the potassium sites along the channel are only 1.4389(2) Å. With the partial occupancy of 0.368(9) for this site, the real distances become longer than two times that number, i.e., 2.8779 Å, but closer to three times that, i.e., 4.3167 Å. The latter is quite normal for K−K. As expected, the thermal ellipsoid for the potassium is extremely anisotropic with U_{33}:U_{11} of ca. 19:1. Figure 3 shows a plane of the Fourier map slicing through the middle of the channel. It can be seen that the electron density along the central line is nearly continuous. It can be called one-dimensional incommensurality, linear amorphousness, or ionic wire. Such "smearing" of electron density and partial occupancy of the cationic site are quite typical for tunnel-like structures with large cations. One such example is the hollandite structure, compounds of which have been studied extensively for possible application as one-dimensional ionic conductors,[6] immobilizors of radioactive waste,[7] and from structural interest toward the cation arrangement in the tunnel.[8] Compounds with this structure are known for all alkali metals, Ba, and Pb,[9] and all of them show similar "elongation" of the cations along the axes of the tunnels. $K_{0.4}Cd_2$ is of a different type tunnel structure but with similar features, and may have similar one-dimensional electronic properties.

The structure of $K_{0.4}Cd_2$ can be compared to some extent with the $CuAl_2$-type structure.[10] The latter includes more than one hundred compounds, mainly binary but also ternary

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Table 3. Selected Bond Lengths (Å) for $K_{0.368(9)}Cd_2$ and $Na_{26}Cd_{141}$

$K_{0.368(9)}Cd_2$

Cd	2 ×	Cd	2.8779(5)
	2 ×	Cd	3.0247(8)
	4 ×	Cd	3.0624(6)
	2 ×	K	3.5040(4)
	4 ×	K	3.7880(4)
K	4 ×	Cd	3.5041(4)
	8 ×	Cd	3.7880(4)
	2 ×	K	1.4389(2)
	2 ×	K	2.8779(5)

$Na_{26}Cd_{141}$

Cd(1)	2 ×	Cd(3)	2.966(2)
	4 ×	Cd(8)	2.9744(8)
	2 ×	Cd(2)	3.010(2)
	2 ×	Cd(10)	3.276(2)
Cd(2)	2 ×	Cd(7)	2.876(2)
	2 ×	Cd(1)	3.010(2)
	4 ×	Cd(8)	3.0493(8)
	2 ×	Cd(10)	3.087(2)
	2 ×	Na(1)	3.838(3)
Cd(3)	2 ×	Cd(6)	2.934(1)
		Cd(1)	2.966(2)
		Cd(4)	3.074(2)
		Cd(3)	3.094(2)
		Cd(3)	3.178(2)
	2 ×	Cd(8)	3.448(1)
	2 ×	Na(2)	3.349(5)
		Na(1)	3.456(8)
Cd(4)	4 ×	Cd(9)	2.878(1)
	2 ×	Cd(3)	3.074(2)
	2 ×	Cd(4)	3.200(2)
	2 ×	Na(4)	3.62(1)
Cd(5)	2 ×	Cd(7)	2.925(1)
		Cd(5)	2.974(2)
	2 ×	Cd(8)	3.024(1)
		Cd(15)	3.031(1)
	2 ×	Cd(11)	3.044(1)
		Cd(6)	3.205(2)
		Na(1)	3.408(2)
	2 ×	Na(3)	3.410(5)
Cd(6)		Cd(12)	2.925(1)
	2 ×	Cd(3)	2.934(1)
	2 ×	Cd(8)	3.055(1)
	2 ×	Cd(11)	3.080(1)
		Cd(9)	3.126(2)
		Cd(5)	3.205(2)
		Na(1)	3.289(6)
	2 ×	Na(2)	3.367(1)
Cd(7)		Cd(2)	2.876(2)
	2 ×	Cd(5)	2.925(1)
	2 ×	Cd(7)	3.028(2)
		Cd(7)	3.107(2)
	2 ×	Cd(8)	3.250(1)
	2 ×	Na(1)	3.319(7)
		Na(3)	3.639(4)
Cd(8)		Cd(11)	2.925(1)
		Cd(1)	2.9744(8)
		Cd(10)	2.9756(9)
		Cd(5)	3.024(1)
		Cd(2)	3.0494(8)
		Cd(6)	3.055(1)
		Cd(7)	3.250(1)
		Cd(14)	3.3807(9)
		Cd(3)	3.448(1)
		Na(1)	3.331(2)
		Na(2)	3.410(5)
		Na(3)	3.497(2)
Cd(9)	2 ×	Cd(4)	2.878(1)
		Cd(12)	2.968(2)
	2 ×	Cd(13)	3.071(1)
		Cd(6)	3.126(2)
	2 ×	Na(2)	3.433(6)
		Na(4)	3.533(4)
Cd(10)	4 ×	Cd(8)	2.9756(9)
	2 ×	Cd(14)	2.976(2)
	2 ×	Cd(2)	3.087(2)
	2 ×	Cd(1)	3.276(2)
	2 ×	Na(3)	3.706(7)
Cd(11)		Cd(14)	2.894(2)
	2 ×	Cd(8)	2.925(1)
		Cd(12)	2.961(2)
	2 ×	Cd(5)	3.044(1)
	2 ×	Cd(6)	3.080(1)
		Cd(11)	3.186(2)
	2 ×	Na(2)	3.337(5)
		Na(3)	3.355(2)
Cd(12)	2 ×	Cd(13)	2.901(2)
	2 ×	Cd(6)	2.925(1)
	2 ×	Cd(11)	2.961(2)
	2 ×	Cd(9)	2.968(2)
	4 ×	Na(2)	3.476(4)
Cd(13)	2 ×	Cd(12)	2.901(2)
	2 ×	Cd(13)	2.925(2)
		Cd(16)	2.925(2)
	4 ×	Cd(9)	3.071(1)
	2 ×	Na(2)	3.494(7)
Cd(14)	2 ×	Cd(11)	2.894(2)
	2 ×	Cd(10)	2.976(2)
	4 ×	Cd(8)	3.3807(9)
		Cd(14)	3.391(3)
	2 ×	Na(3)	3.260(8)
		Na(2)	3.575(7)
Cd(15)	6 ×	Cd(5)	3.031(1)
	3 ×	Na(3)	3.366(9)
Cd(16)	6 ×	Cd(13)	2.925(2)
	2 ×	Na(4)	3.12(2)
Na(1)	2 ×	Cd(6)	3.289(6)
	4 ×	Cd(7)	3.319(7)
	4 ×	Cd(8)	3.331(2)
	2 ×	Cd(3)	3.456(8)
	2 ×	Cd(5)	3.408(2)
	2 ×	Cd(2)	3.838(3)
Na(2)	2 ×	Cd(11)	3.337(5)
	2 ×	Cd(3)	3.349(5)
	2 ×	Cd(6)	3.367(1)
	2 ×	Cd(8)	3.410(5)
	2 ×	Cd(9)	3.433(6)
	2 ×	Cd(12)	3.476(4)
		Cd(13)	3.494(7)
		Cd(14)	3.575(7)
		Na(2)	3.865(2)
Na(3)	2 ×	Cd(14)	3.260(8)
	2 ×	Cd(11)	3.355(2)
		Cd(15)	3.366(9)
	4 ×	Cd(5)	3.410(5)
	4 ×	Cd(8)	3.497(2)
	2 ×	Cd(7)	3.639(4)
	2 ×	Cd(10)	3.706(7)
Na(4)		Cd(16)	3.12(2)
	6 ×	Cd(9)	3.533(4)
	6 ×	Cd(4)	3.62(1)
		Na(4)	3.38(5)

intermetallics.[11] The two structures belong to the same space group, and have the same site for the B element, i.e., Cd or Al. Nevertheless, they have very different *c/a* ratios, 0.3139 for $K_{0.4}Cd_2$ and between 0.7431 and 0.8810 for the $CuAl_2$-type. This leads to a very different coordination around the crystallographically equivalent site. Each B atom in $CuAl_2$ has 11 other B neighbors, while they are only 8 in $K_{0.4}Cd_2$. The site of the A atoms is different for the two structures as well. While potassium in $K_{0.4}Cd_2$ is at the 4*c* position (0, 0, 0 and 0, 0, $^1/_2$), the A atom in the $CuAl_2$-type structures is at the 4*a* site (0, 0, 1/4 and 0, 0, 3/4). This means that the A atom in the latter centers a square antiprism with eight equidistant B neighbors. Another significant difference between the two structures is the type of the A element. None of the $CuAl_2$-type compounds involves alkali metal at that site. It is rather an element with similar size and electronegativity as the B element, and unlike K in $K_{0.4}Cd_2$ it can eventually participate in more or less covalent interactions. A study on the $CuAl_2$-type compounds shows that the atomic radii ratio of A and B is in a relatively small range, 0.66−0.87.[10] That ratio for $K_{0.4}Cd_2$ is significantly larger, 1.37. Also, in most of the $CuAl_2$ compounds the A element is the more electronegative element while potassium in $K_{0.4}Cd_2$ is the less electronegative element by far, by 0.87.

Further comparison of the cadmium framework can be made with parts of the framework of La_3In_4Ge.[12] It has a structure related to another very popular structural type among the intermetallics, that of Cr_5B_3.[13] The compound has very similar

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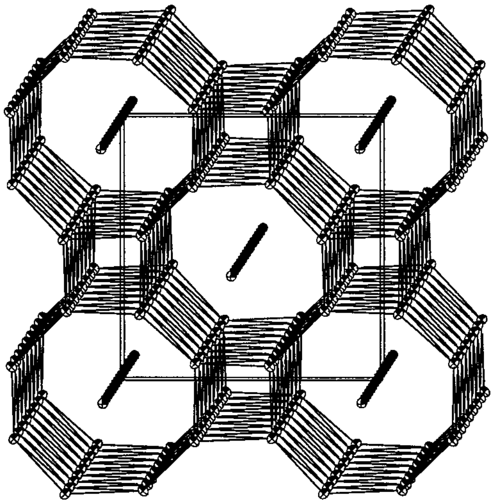

Figure 1. ORTEP drawing of the structure of $K_{0.4}Cd_2$ (30% thermal ellipsoids) with a view along the *c* axis of the body-centered tetragonal cell (outlined). Bonds are drawn between the cadmium atoms, while the potassium cations are shown as isolated spheres within the octagonal channels. Although only ca. 40% of the potassium sites are taken by potassium cations, they are all shown as occupied (see the text).

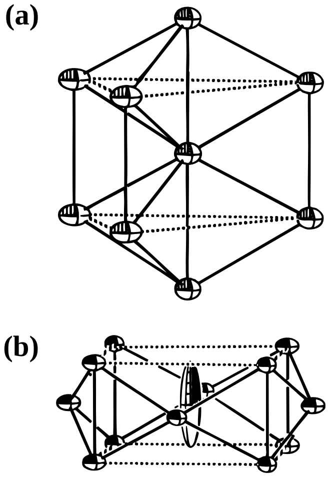

Figure 2. ORTEP drawings (70% thermal ellipsoids) of the cadmium coordination around (a) cadmium and (b) potassium in $K_{0.4}Cd_2$. Each cadmium atom is 8-bonded within a bicapped trigonal prism, while each potassium has 12 cadmium neighbors forming a tetracapped square prism.

eight-membered rings but they are not continuous. The channels are found in slabs of $LaIn_4$ that are separated and "blocked" by well-packed layers of La_2Ge.

The present K−Cd phase diagram indicates only one known compound in the system, KCd_{13}, and quite a large unknown section on the potassium-rich side that has been only traced. There is an eutectic shown at ca.15 atom % of K, and this is close to the concentration of potassium in $K_{0.4}Cd_2$. Perhaps there is an eutectic somewhere between KCd_{13} and $K_{0.4}Cd_2$, but somewhat shifted toward lower potassium concentrations. Our extensive studies of the system show that there are no other K−Cd compounds (stable at normal conditions).

The "replacement" of potassium by sodium results in a completely different structure for the same stoichiometry. ($Na_{26}Cd_{141}$ can be written as $Na_{0.369}Cd_2$.) The new compound $Na_{26}Cd_{141}$ has a structure that is more typical for intermetallics. It is more three-dimensional, better packed, and with higher coordination numbers of the atoms. All cadmium atoms are heavily interlinked with 6, 8, 9, and 10 neighbors. Structurally $Na_{26}Cd_{141}$ is very close to a compound with quite different composition and types of elements, $Y_{26}Pd_{80}Sn_{62}$.[14] The two differ also in the numbers of atoms, i.e., 141 cadmium atoms in $Na_{26}Cd_{141}$ versus 142 palladium and tin atoms in the latter. One atom in the cadmium compound occupies a position of lower multiplicity (1*b* instead of 2*c*). The structure of $Y_{26}Pd_{80}Sn_{62}$ has been described as built of intergrown $CaCu_5$- and $MnCu_2Al$-type segments.[14] Three types of layers ordered along *c* in an ABCBA sequence can be used to view the anionic framework formed by the cadmium atoms in $Na_{26}Cd_{141}$ (Figure 4). The layers A and C are flat, while B is puckered with an amplitude of about ±1 Å and connects the other two. This approach is to help in the visualization of the structure only, and in no way implies a layered structure. Thus, distances between atoms of different layers are comparable with those within the layers.

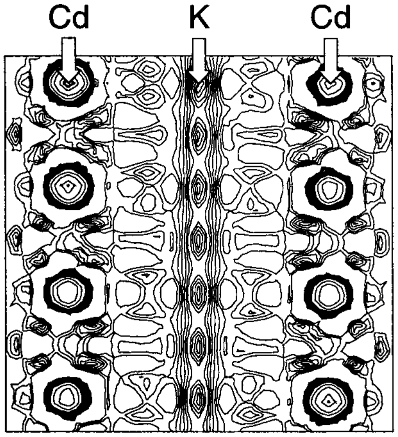

Figure 3. Plane of the Fourier map through the channel in $K_{0.4}Cd_2$ (*c* is vertical). The electron density is nearly continuous along the central line where potassium is refined with 36.8(9)% occupancy. Shown by arrows are the positions of the cadmium and potassium.

It is interesting to compare $Na_{26}Cd_{141}$ with Na_2Cd_{11}, one of the two known compounds in the system (the other one is $NaCd_2$).[15] The sodium-to-cadmium ratios, 0.184 and 0.182 for $Na_{26}Cd_{141}$ and Na_2Cd_{11}, respectively, are strikingly close. This may suggest structural similarities, and may raise suspicions about the accuracy of the structure determinations of one or both compounds. Moreover, various compositions had been assigned to the cadmium-richest compound in the past, i.e., before the structure and therefore the composition of Na_2Cd_{11} were known.[16] It was conceivable that the compound is one and the same but structurally mishandled either before or during the present structural determination. There is also a possibility for polymorphic relation between the two, i.e., stability at different temperature regions. Nevertheless, the two compounds differ in stoichiometry, and are structurally very different. Na_2Cd_{11} has been seen many times as a minor phase in many of our reactions, and it has a distinctively different powder diffraction pattern from that of $Na_{26}Cd_{141}$. The latter is observed only in reactions loaded as $NaCd_5$, heated and then quenched in liquid nitrogen. This can mean that $Na_{26}Cd_{141}$ melts incongruently. It is so close to the congruently melting Na_2Cd_{11} that slow cooling will always favor the latter. The Na−Cd phase diagram has two congruently melting compounds, Na_2Cd_{11} and $NaCd_2$ melting at 363 and 384 °C, respectively. There is an

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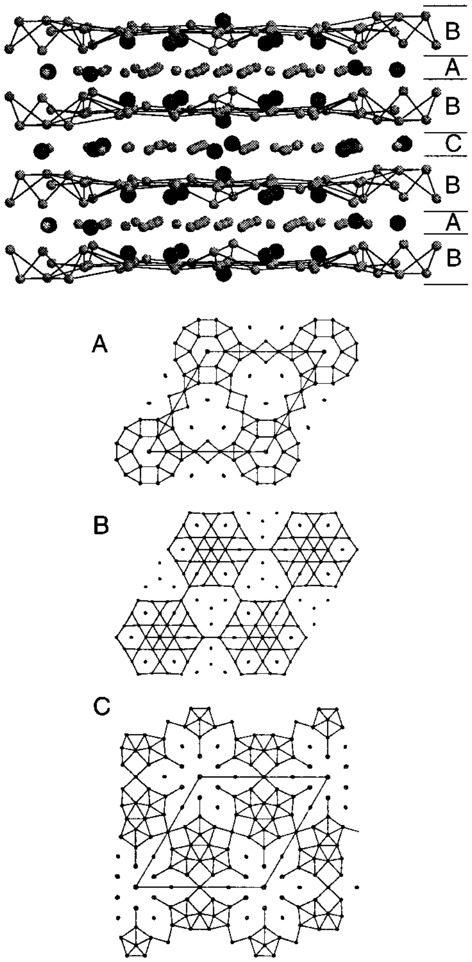

Figure 4. General view of the structure of $Na_{26}Cd_{141}$ (top) with cadmium and sodium shown as small gray and large black spheres, respectively (c is vertical). The structure can be viewed as built of three different layers A, B, and C stacked along c in the order ABCBA. For clarity all interlayer Cd−Cd bonds have been omitted. Shown also are views along c of the three layers labeled with the corresponding letters.

eutectic at 348 °C between them at 21.5 atom % of sodium. This means that the peritectic temperature for $Na_{26}Cd_{141}$ must be somewhere between 348° and 363 °C, which makes the compound very "mildly" peritectical. It is paramagnetic according to the measured magnetic susceptibility.

Electronic Structure. Extended-Hückel band calculations were performed on the cadmium part of $K_{0.4}Cd_2$. (Due to software limitations in the number of atoms and orbitals, such calculations were not carried out for $Na_{26}Cd_{141}$.) The procedures and parameters have been described in detail elsewhere.[3] All distances around cadmium are either along c or have a major component along that axis. The components in the ab plane are small since cadmium has no neighbors within or close to that plane. This, of course, leads to weaker interactions in the plane and much stronger ones along c. This is clearly manifested by the band structure of $K_{0.4}Cd_2$ (Figure 5) which shows much greater dispersion of the bands along that axis or directions close to it. The X → Γ and Z → L directions can be associated with interactions within the ab plane while Γ → Z reflects interactions in the chain of Cd atoms along c. The direction L → Γ runs along the body diagonal of the first Brillouin zone and characterizes interactions that are mostly between cadmium atoms of the trigonal prism and the central cadmium. The plot shows two very important features. First, due to strong p_z and s interactions the Γ → Z and L → Γ directions are much more dispersed compared to X → Γ and Z → L. Second, the Fermi level crosses many of the dispersed bands, i.e., the bands along c. This leads to a complex Fermi surface with several closed and warped parts which makes very unlikely any Fermi surface driven instabilities. The partially filled bands and the complex Fermi surface suggest metallic character of the compound and no anomalies in the magnetic susceptibility. This is in agreement with the magnetic measurements which show temperature independent magnetic susceptibility in the temperature range 50−295 K.

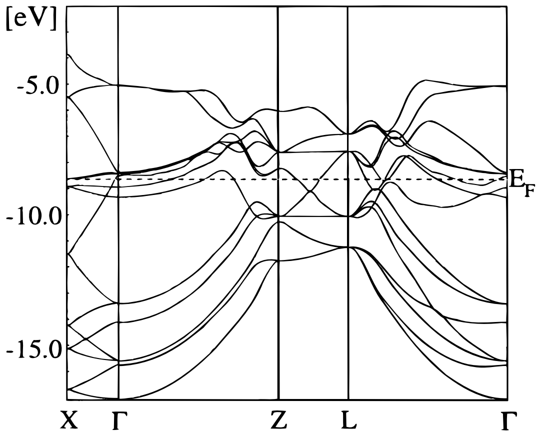

Figure 5. Shown is the band diagram of the cadmium framework in $K_{0.4}Cd_2$ calculated by the extended Hückel method. X, Z, and L correspond to the k points (0.5, 0, 0), (0, 0, 0.5), and (0.5, 0.5, 0.5).

The two compounds $A_{0.4}Cd_2$ belong to significantly different structural types. The size and the electronegativity of the cation clearly play important roles in defining the structure. This has been previously discussed in terms of the "solvating" power of the cations,[17] and for the compounds ATl (A = Na, K, Rb, Cs) this effect can be traced more quantitatively due to the simpler structures.[18]

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure determinations of $K_{0.4}Cd_2$ and $Na_{26}Cd_{141}$ is available on the Internet only. Access information is given on any current masthead page.

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