Spin ladder compound Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$: synthesis and investigation

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The complex oxide Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$ was synthesized and investigated by means of X-ray powder diffraction, electron diffraction, magnetic susceptibility measurements and band structure calculations. Its structure is similar to that of MV$_2$O$_5$ compounds (M = Na, Ca) giving rise to a spin system of coupled $S = 1/2$ two-leg ladders. Magnetic susceptibility measurements reveal a spin gap-like behavior with $\Delta \approx 270$ K and a spin singlet ground state. Band structure calculations suggest Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$ to be a system of weakly coupled dimers in perfect agreement with the experimental data. Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$ provides an example of the modification of the spin system in layered vanadium oxides by cation substitution. Simple correlations between the cation size, geometrical parameters and exchange integrals for the MV$_2$O$_5$-type oxides are established and discussed.

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I. INTRODUCTION

Complex vanadium oxides often present attractive examples of low-dimensional magnetic systems and exhibit unusual phenomena like spin gap formation or a spin liquid ground state. These phenomena are not fully understood yet, therefore the search and investigation of novel compounds revealing low-dimensional spin systems is still a challenging task for solid state physics. Basically, there are two possible ways to search for new spin systems. The first way deals with the study of new structural types that are completely different from those of well-known and thoroughly investigated compounds. The second way suggests a systematic investigation of a number of related compounds. Both ways have been successfully realized during the last decade. However, the search for new structural types requires substantial intuition and luck. Systematic studies are more predictable if one can understand the relationship between the composition, crystal structure of the solid and the magnetic interactions in it.

MV$_2$O$_5$ compounds (M is an alkaline or alkaline-earth metal) are promising candidates for a systematic study of magnetic interactions in vanadium oxides. All of them (except for that with M = Cs) have layered structures with layers formed by edge- and corner-sharing VO$_5$ square pyramids (see Fig. 1). The M cations are situated between the layers. If M is a monovalent cation the average oxidation state of vanadium is +4.5 and both charge ordered (LiV$_2$O$_5$) or disordered (NaV$_2$O$_5$ above 35 K) states may be realized along with 1D magnetic behavior. Actually, the properties of NaV$_2$O$_5$ are even more complicated since different patterns of charge ordering have been recently found for this compound at low temperature.

The physics of MV$_2$O$_5$ compounds with divalent M cations (Ca, Mg) is simpler due to the absence of charge degrees of freedom. In both oxides vanadium atoms are tetravalent and a system of coupled $S = 1/2$ two-leg spin ladders is realized. However, exchange interactions in CaV$_2$O$_5$ and MgV$_2$O$_5$ are quite different. In CaV$_2$O$_5$ the strongest interaction runs along the rung of the lad-

![FIG. 1: (Color online) The projection of the Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$ crystal structure along the c axis (upper panel) and the system of coupled two-leg spin ladders (lower panel). In the upper panel circles denote the mixed Pb/Cd position, white arrows show three different nearest-neighbor exchange interactions. In the lower panel solid lines correspond to the legs of the ladders, dashed lines show the rungs and dots indicate inter-ladder coupling. The inter-layer hopping $t_\perp$ is not shown.](image-url)
nder \((J_1 \approx 600 \text{ K}, \text{see Fig. 1})\) while other interactions \((J_2, J_3, J_4)\) do not exceed \(100 - 150 \text{ K}\) \cite{11,12,13,14}. Thus, weakly coupled spin dimers are formed and \(\text{CaV}_2\) reveals a spin gap \(\Delta \approx J_1\) [experimental values of \(\Delta\) range from 560 to 660 K (Refs. 14, 15, 16)]. In contrast, \(\text{MgV}_2\) reveals comparable nearest-neighbor interactions \(J_1, J_2, J_3\) of about \(100 \text{ K}\) \cite{11,12}. The presence of a spin gap in \(\text{MgV}_2\) is still argued and the suggested values of \(\Delta\) are quite small \((15 - 20 \text{ K})\) \cite{16,17,18,19}. The change of \(\text{V–O–V}\) angles has been claimed in Ref. 11 as the main reason for the differences between \(\text{CaV}_2\) and \(\text{MgV}_2\).

A general phase diagram for the coupled \(S = 1/2\) two-leg spin ladders is rather complicated revealing unusual ground states (namely, spiral order) and a number of quantum critical points. However, most of the regions of this diagram still lack experimental study. The remarkable difference between the magnetic properties of \(\text{CaV}_2\) and \(\text{MgV}_2\) suggests that an appropriate substitution in the \(M\) cation position of \(\text{MV}_2\) – an example of \(\text{MV}_2\) – modifies the spin system and to shift between different regions of the phase diagram. Here we present the results of synthesis and investigation of \(\text{Pb}_{0.55}\text{Cd}_{0.45}\text{V}_2\text{O}_5\) – an example of \(\text{MV}_2\)-type compounds combining two different cations in the \(M\) position. The joint experimental and computational study of \(\text{Pb}_{0.55}\text{Cd}_{0.45}\text{V}_2\text{O}_5\) allows us to carry out a comparison between several \(\text{MV}_2\)-type compounds and to establish correlations between the cation size, geometrical parameters and exchange integrals.

II. METHODS

A powder sample of \(\text{Pb}_{0.55}\text{Cd}_{0.45}\text{V}_2\text{O}_5\) was obtained by heating a mixture of \(\text{Pb}_2\text{V}_2\text{O}_7, \text{CdO}, \text{V}_2\text{O}_3\) and \(\text{V}_2\text{O}_5\) (ratio 2:4:1:1) in an evacuated and sealed silica tube at 700\(^\circ\)C for 24 hours. A change in the \(\text{Pb}:\text{Cd}\) ratio always resulted in the appearance of trace amounts of impurity phases in the samples. A change of heating conditions was used to establish correlations between the cation size, geometrical parameters and exchange integrals.

TABLE I: Atomic coordinates and isotropic thermal displacement parameters for \(\text{Pb}_{0.55}\text{Cd}_{0.45}\text{V}_2\text{O}_5\).

| Atom | Site | Occupancy | \(x\) | \(y\) | \(z\) | \(U_{iso}\) (\(\text{Å}^2\)) |
|------|------|-----------|------|------|------|------------------|
| Pb   | 2b   | 0.55(1)   | 0.75 | 0.25 | 0.1557(1) | 0.0122(4)        |
| Cd   | 2b   | 0.45(1)   | 0.75 | 0.25 | 0.1557(1) | 0.0122(4)        |
| V    | 4f   | 1         | 0.4063(1) | 0.25 | 0.3883(4) | 0.0076(7)        |
| O(1) | 4f   | 1         | 0.3884(3) | 0.25 | 0.0621(8) | 0.008(1)         |
| O(2) | 4f   | 1         | 0.5733(4) | 0.25 | 0.4732(8) | 0.008(1)         |
| O(3) | 2a   | 1         | 0.25   | 0.25 | 0.549(1)  | 0.008(1)         |

III. RESULTS

A. Crystal structure

\(\text{Pb}_{0.55}\text{Cd}_{0.45}\text{V}_2\text{O}_5\) has an orthorhombic unit cell with lattice parameters \(a = 11.3565(2) \text{ Å}, b = 3.6672(1) \text{ Å}, c = 4.9017(1) \text{ Å}\). Single crystals of \(\text{Pb}_{0.55}\text{Cd}_{0.45}\text{V}_2\text{O}_5\) cannot be obtained since above 700\(^\circ\)C the compound gradually decomposes without melting. Therefore, the XPD data were used for the structural study.

The lattice parameters for \(\text{Pb}_{0.55}\text{Cd}_{0.45}\text{V}_2\text{O}_5\) and \(\text{CaV}_2\text{O}_5\) \((a = 11.351 \text{ Å}, b = 3.604 \text{ Å}, c = 4.893 \text{ Å}\), space group \(Pmnn\)\(^{15}\)\) are rather close, therefore we used the crystal structure of \(\text{CaV}_2\text{O}_5\) as an initial model for the Rietveld refinement. Indexing of XPD and ED (see below) patterns revealed only the reflection conditions \(hk0, h + k = 2n\) indicating two possible space groups: \(Pmnn\) and \(P2_1mn\), a subgroup of \(Pmnn\). The lead and cadmium atoms were placed into \(2b\) position (corresponding to calcium in \(\text{CaV}_2\text{O}_5\)) and occupancy factors \(g_{\text{pb}} = g_{\text{Cd}} = 0.5\) were set.

The refinement in both \(Pmnn\) and \(P2_1mn\) space groups gave similar results, therefore the highest possible symmetry (\(Pmnn\)) was chosen for the final refinement. The atomic displacement parameters of all oxy-
gen atoms were constrained. Anisotropic strain broadening for the profile function was refined to achieve a proper fit for all reflections in the XPD pattern. Finally, occupancy factors of lead and cadmium atoms were also refined with a constraint \( g_{\text{Pb}} + g_{\text{Cd}} = 1 \) yielding \( g_{\text{Pb}} = 0.55(1), g_{\text{Cd}} = 0.45(1) \) and the Pb\(_{0.55}\)Cd\(_{0.45}\)V\(_2\)O\(_5\) composition. This composition is in a good agreement with the EDXS result Pb:Cd:V = 1.2(1):1.0(1):3.8(1) but slightly differs from the initial Pb\(_{0.55}\)Cd\(_{0.45}\)V\(_2\)O\(_5\) composition. This indicates the presence of an amorphous component in the sample under investigation.

The crystal structure of Pb\(_{0.55}\)Cd\(_{0.45}\)V\(_2\)O\(_5\) is shown in Fig. 1. The experimental, calculated and Rietveld plots are shown in Fig. 2. Table I presents atomic coordinates and thermal displacement parameters, while Table II summarizes the main interatomic distances and angles in the crystal structure. The final residuals of the refinement are \( R_p = 0.022, R_F = 0.020 \), and \( \chi^2 = 1.29 \).

The crystal structure of Pb\(_{0.55}\)Cd\(_{0.45}\)V\(_2\)O\(_5\) is very similar to that of CaV\(_2\)O\(_5\). Vanadium atoms form VO\(_5\) square pyramids with one short vanadyl bond and four longer equatorial bonds typical for tetravalent vanadium. The V\(^{4+}\)O\(_5\) square pyramids with opposite orientation of vanadyl bonds are linked into zigzag chains via common edges. The pyramids in neighboring chains share their corners and form [V\(_2\)O\(_5\)] layers. Lead and cadmium atoms randomly occupy one crystallographic position between the vanadium-oxygen layers. The M–O distances are rather short for lead due to the presence of the smaller cadmium cation in the same position.

Lead and cadmium cations are fairly different in size (ionic radii 1.45 Å and 1.21 Å, respectively), therefore one would expect cation ordering in Pb\(_{0.55}\)Cd\(_{0.45}\)V\(_2\)O\(_5\) resulting in a decrease of symmetry and superstructure formation. However, all ED patterns (Fig. 3) could be indexed in the \( Pmmn \) space group with the cell parameters found from the XPD data. The appearance of the forbidden reflections \( h00 : h \neq 2n \) in the [011] zone is due to double diffraction since these reflections disappear after rotating the crystal away from the perfect orientation. Thus, one may conclude that lead and cadmium atoms in Pb\(_{0.55}\)Cd\(_{0.45}\)V\(_2\)O\(_5\) are randomly distributed.

We also prepared Pb\(_{1-x}\)Cd\(_{x}\)V\(_2\)O\(_5\) samples with \( 0 \leq x \leq 1 \). The MV\(_2\)O\(_5\)-type phase was detected for \( 0.3 \leq x \leq 0.7 \), but single phase samples were obtained only for \( x = 0.5 \). The lattice parameters for the CaV\(_2\)O\(_5\)-type phase were almost identical to those refined for Pb\(_{0.55}\)Cd\(_{0.45}\)V\(_2\)O\(_5\). Thus, the Pb\(_{0.55}\)Cd\(_{0.45}\)V\(_2\)O\(_5\) phase has no considerable homogeneity range.

### B. Magnetic susceptibility

The \( \chi(T) \) curve of Pb\(_{0.55}\)Cd\(_{0.45}\)V\(_2\)O\(_5\) (Fig. 4) reveals a broad maximum, typical for low-dimensional spin systems. The fast decrease of the susceptibility below the maximum may be indicative of a spin gap while the upturn below 30 K is usually attributed to the paramagnetic impact of impurities and defects. In general, the \( \chi(T) \) curve of Pb\(_{0.55}\)Cd\(_{0.45}\)V\(_2\)O\(_5\) is similar to that for CaV\(_2\)O\(_5\). Nevertheless, in CaV\(_2\)O\(_5\) the susceptibility maximum is at \( T_{\text{max}} \approx 350 \) K while in the case of Pb\(_{0.55}\)Cd\(_{0.45}\)V\(_2\)O\(_5\) \( T_{\text{max}} \) is half this value (about 170 K). The position of the susceptibility maximum is usually

![FIG. 2: (Color online) Experimental, calculated and difference XRD patterns for Pb\(_{0.55}\)Cd\(_{0.45}\)V\(_2\)O\(_5\). The halo in the XPD pattern at \( 2\theta = 15 \sim 25^\circ \) indicates the presence of an amorphous impurity in the sample under investigation.](image-url)

![FIG. 3: Electron diffraction patterns along the [001] and [011] directions.](image-url)

| TABLE II: Selected interatomic distances (in Å) and angles (in deg). M denotes the mixed Pb/Cd position |
|-----------------------------------------------|
| M–O(1) | 4 × 2.639(3) | V–O(1) | 1.614(5) |
| M–O(2) | 2 × 2.540(4) | V–O(2) | 1.942(5) |
| M–O(3) | 2 × 2.336(4) | V–O(3) | 2 × 1.969(2) |
| V–O(2)–V (\( J_2 \)) | 137.3(2) | V–O(2)–V | 100.88(14) |
| V–O(3)–V (\( J_1 \)) | 132.1(3) | | |
there are two vanadium atoms per formula unit. We
susceptibility with the isolated dimer model. The inset shows the intrinsic susceptibility $\chi_{\text{int}}$ of Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$: $\chi_{\text{int}} = \chi_{\text{exp}} - \chi_0 - C/T$ (see equation 1).

A characteristic of the strongest exchange interaction in the system. Therefore one may suppose that the spin systems of Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$ and CaV$_2$O$_5$ are qualitatively similar, but a slight change of the crystal structure results in a weakening of the magnetic interactions.

CaV$_2$O$_5$ is considered to be a system of weakly coupled dimers, therefore we follow Ref. 13 and fit the experimental curve in Fig. 3 with the expression

$$\chi = \chi_0 + C/T + \frac{Ng^2\mu_B^2}{k_BT} \frac{1}{e^{\Delta/k_BT} + 1}$$ (1)

where $\chi_0$ is a temperature-independent term, $C/T$ corresponds to the paramagnetic signal of defects (impurities) while the last term corresponds to a system of isolated dimers. $\Delta$ is the spin gap value and $N = 2N_A$ since there are two vanadium atoms per formula unit. We found a good fit with $\chi_0 = 4.0(1) \times 10^{-4}$ emu/mol, $C = 3.1(1) \times 10^{-3}$ emu-K/mol, $g = 1.55(2)$, $\Delta = 270.7(3)$ K. The $g$ value is somewhat lower than one can expect for V$^{4+}$ ($g = 1.93 - 1.96$, see, for example, Ref. 20). The underestimate of $g$ may be caused by the presence of the amorphous impurity in the samples under investigation. According to XRD (see above) the samples contain an appreciable ($\sim 25\%$) amount of the amorphous component that may really lead to an error in the sample weight and result in the decrease of $g$. The deviation of the spin system of Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$ from the simple dimer model may be another reason for the decrease of $g$. However, the influence of this factor is much weaker than that of the amorphous component. We are convinced that a spin dimer model is the best choice for the reliable fitting of the present experimental data, since the use of the improved model (including four exchange integrals, see [11C]) makes the fit very unstable.

The subtraction of $\chi_0$ and of the paramagnetic contribution $C/T$ shows that the intrinsic susceptibility of Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$ drops down to zero at low temperatures (see the inset of Fig. 4) indicating a spin singlet ground state.

C. Band structure and exchange interactions

Fitting of experimental data provides a phenomenological way to study magnetic interactions. However, the crystal structure of Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$ results in a rather complicated spin system with several different types of nearest-neighbor interactions (see Fig. 2), therefore a mere phenomenological description of the system may appear unreliable. A microscopic picture will provide additional information about exchange interactions in the system.

A direct estimate of the exchange interactions can be derived on the basis of band structure data. The latter one is usually obtained by density-functional calculations. However, there is an additional difficulty in case of Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$ since lead and cadmium atoms randomly occupy one crystallographic position. Sophisticated techniques (like CPA, VCA) or supercell calculations are required to treat correctly such type of disorder. Nevertheless, one may try a more simple way in order to study exchange interactions in Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$. According to the recent study of CaV$_2$O$_5$ and MgV$_2$O$_5$, the exchange integrals in these compounds are not sensitive to the type of metal cation (Ca or Mg) but depend on the geometry of the [V$_2$O$_5$] layer (namely, V–O–V angles). Therefore, we used the structural parameters of Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$ (Table 1) but set the occupancy factors $g_{\text{Pb}} = 1$, $g_{\text{Cd}} = 0$, or vice versa. Thus, the band structure for the two hypothetical compounds (PbV$_2$O$_5$ and CaV$_2$O$_5$)...
FIG. 6: (Color online) Band structure of PbV$_2$O$_5$ and CdV$_2$O$_5$. Solid lines show the fit of the tight-binding model to the LDA energy spectra of insulating transition metal compounds are character with an admixture of oxygen. Note that gapless energy bands formed by oxygen orbitals and provide the bonding between them in Fig. 5. The states below CdV$_2$O$_5$ panel) and CdV$_2$O$_5$ dots indicate the contribution of the V $3d_{xy}$ states. Thick solid lines show the fit of the tight-binding model to the LDA band structure.

The density of states (DOS) plots for PbV$_2$O$_5$ and CdV$_2$O$_5$ are very similar, therefore we show only one of them in Fig. 5. The states below $-2$ eV are mainly formed by oxygen orbitals and provide the bonding between vanadium, lead or cadmium and oxygen. The highest occupied states have predominantly vanadium character with an admixture of oxygen. Note that gapless energy spectra of insulating transition metal compounds are a typical failure of LDA due to an underestimate of strong electron-electron correlations in the V $3d$ shell. The energy gap is readily reproduced by means of LSDA+$U$ (see, for example, Ref. 11).

According to simple crystal field considerations, the lowest (and hence occupied) vanadium $3d$ orbital in the V$^{4+}$O$_5$ square pyramid is the $d_{xy}$ one. There are four vanadium atoms in the unit cell of Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$, therefore we find near the Fermi level four bands formed by V $d_{xy}$ orbitals (Fig. 6). These bands are suitable for the tight-binding fit.

Similar four-band tight-binding models were constructed for both PbV$_2$O$_5$ and CdV$_2$O$_5$. The leading interactions of the models are shown in Fig. 1. A number of long-range interactions were also included in the model in order to provide a proper fit. Hopping parameters $t$ corresponding to the main interactions are listed in Table III. Other $t$s were found to be less than 0.020 eV, therefore one can neglect them while considering the overall magnetic behavior of the spin system.

The hopping parameters of PbV$_2$O$_5$ and CdV$_2$O$_5$ are quite similar. If one considers the spin lattice in terms of coupled ladders, then the largest hopping ($t_1$) corresponds to the rungs of the ladders. Other nearest-neighbor hoppings are about half this value. The significant difference between the values of $t_2$ and $t_4$ for PbV$_2$O$_5$ and CdV$_2$O$_5$ may be caused by the influence of the metal cation on the corresponding interactions. Nevertheless, the basic feature of the magnetic interactions in both compounds is the same: strong coupling along the rungs of the ladder. Now, the $t$ values can be averaged and antiferromagnetic contributions to the exchange integrals are estimated as $J_{1}^{AFM} = 4t_i^2/U$ where $U$ is the effective on-site Coulomb repulsion.

In general, one should also take into account ferromagnetic contributions since $J_{1} = J_{1}^{FM} + J_{1}^{AFM}$. Unfortunately, the estimation of $J_{1}^{FM}$ implies LSDA$+U$ calculation, and the latter one is a difficult task for a partially disordered structure of Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$. According to Refs 11,12 ferromagnetic interactions in layered vanadium oxides are relatively weak. For that reason we neglect $J_{1}^{FM}$ and assume that $J_{1} = J_{1}^{AFM}$. Remarkable agreement between experimental and calculated values of $J_{1}$ (see below) a posteriori justifies this approach.

We set $U = 3.6$ eV according to Ref. 11 and find $J_{1}^{AFM} = 303$ K. This value may be compared with the spin gap $\Delta \approx 270$ K found by our fit of the susceptibility curve. In case of isolated dimers the spin gap is equal to the intradimer interaction and $J_{1} \approx \Delta \approx 270$ K in perfect agreement with the computational result. Other nearest-neighbor interactions are at least four times weaker than $J_{1}$, hence Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$ may be considered as a system of weakly coupled dimers. The interlayer coupling is very weak ($J_{\perp} \approx 3$ K) as one can expect for the layered structure with the magnetically active $d_{xy}$ orbitals parallel to the layers.

|                  | $t_1$ | $t_2$ | $t_3$ | $t_4$ | $t_{\perp}$ |
|------------------|-------|-------|-------|-------|-------------|
| PbV$_2$O$_5$     | 159   | 63    | 72    | 57    | -17         |
| CdV$_2$O$_5$     | 147   | 26    | 52    | 98    | -14         |
| Averaged         | 153   | 44.5  | 62    | 77.5  | -15.5       |
| (K)              | $J_1$ | $J_2$ | $J_3$ | $J_4$ | $J_{\perp}$ |
|                  | 303   | 26    | 50    | 78    | 3           |
IV. DISCUSSION

Experimental and computational data clearly show that Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$ is similar to CaV$_2$O$_5$ and reveals a spin system of weakly coupled dimers. However, the intradimer interactions in these compounds differ by a factor of two. Now we will try to uncover a structural evidence of this change. The comparison of Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$ with two known MV$_2$O$_5$ compounds (M = Ca, Mg) allows us to establish reliable correlations between exchange integrals and geometrical parameters.

The various magnetic interactions in the MV$_2$O$_5$-type compounds have different origin. $J_1$ and $J_2$ run via V–O–V superexchange paths. $J_3$ is a superposition of direct V–V exchange and 90° V–O–V superexchange. $J_4$ corresponds to a more complicated superexchange path that involves two oxygen atoms and probably the Mg cation as well. Further we will focus on $J_1$ and $J_2$ since only single V–O–V paths may provide reasonably simple correlations between exchange integrals and geometrical parameters. In general, such paths are characterized by three parameters: V–O–V angle and two corresponding V–O distances. In MV$_2$O$_5$ compounds the parameters are related, therefore two parameters are sufficient: the angle and one distance (V–O or V–V). The geometrical parameters corresponding to $J_1$ and $J_2$ are listed in Table III.

The values in Table III are easily understood if one considers the change of the crystal structure caused by the decrease of the cation size. In CaV$_2$O$_5$, calcium (ionic radius $r = 1.26$ Å) has eight-fold coordination and the [V$_2$O$_5$] layers are flat. Smaller cations like magnesium ($r = 1.03$ Å) require a decrease of the coordination number (six in case of Mg) that is achieved by the corrugation of the layers (see Fig. 7). Edge-sharing connections of the square pyramids are rigid in contrast to corner-sharing ones, therefore the corrugation of the layers results in a significant change of the V–O(3)–V angle. The averaged ionic radius of the effective “Pb$_{0.55}$Cd$_{0.45}$” cation (1.33 Å) is even larger than that of calcium and the layers remain flat. For that reason, angles remain almost constant but V–V distances (and hence V–O distances) increase.

Now we turn to the exchange integrals. According to Ref. [1] the dramatic decrease of $J_1$ in MgV$_2$O$_5$ compared to that in CaV$_2$O$_5$ is caused by the decrease of the V–O(3)–V angle. In case of Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$ the decrease of $J_1$ is less pronounced since interatomic distances are changed instead of the angle. This result is quite reasonable as magnetic interactions are known to be far more sensitive to the variation of angles than to interatomic distances.

The values of $J_2$ are more difficult to explain. The relevant bonding angles in the two compounds are quite similar. The V–V distance in MgV$_2$O$_5$ and Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$ is higher than in CaV$_2$O$_5$ but $J_2$(MgV$_2$O$_5$) ≈ $J_2$(CaV$_2$O$_5$) ≫ $J_2$(Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$). One may suggest two reasons for such changes of $J_2$. First, tight-binding model reveals significant next-nearest-neighbor “diagonal” interaction ($J_1 \approx 80$ K) in Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$ while lower estimates ($J_1 \approx 20$ K) were given for CaV$_2$O$_5$ and MgV$_2$O$_5$ [11, 12]. This explanation seems to be reasonable (at least qualitatively) since lead and cadmium have different relevant orbitals compared to calcium or magnesium. Therefore, Pb and Cd may mediate superexchange interactions better. Note however that we discuss antiferromagnetic contributions to the exchange integrals only (see Band structure section), and ferromagnetic contributions may slightly change the situation. Second, the consideration of the geometrical parameters corresponding to V–O–V path only may be an oversimplification as other factors (e.g. local environment of vanadium: all the V–O distances and O–V–O angles) are also important.

Thus, in case of complex superexchange paths it is difficult to impose a simple correlation between exchange integrals and geometrical parameters as the spin system in the MV$_2$O$_5$-type compounds is rather complicated. Nevertheless, we succeed in the explanation of the basic difference between Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$ and CaV$_2$O$_5$. We found that the CaV$_2$O$_5$ structure is conserved rather well and the increase of the effective cation size in Pb$_{0.55}$Cd$_{0.45}$V$_2$O$_5$ results in a mere increase of interatomic distances. Both $J_1$ and $J_2$ are decreased and the type of the spin system (weakly coupled dimers) remains...
unchanged.

The corrugation of the \([V_2O_3]\) layer (alike the one that happens in \(MgV_2O_5\) would be necessary to induce a really significant change of the spin system. The layers in \(CaV_2O_5\) are almost flat and the further increase of the cation size can not give rise to their distortion. It means that one has to introduce a smaller (namely, smaller than calcium) cation between the \([V_2O_5]\) layers in order to achieve an appreciable change of the spin system. The number of the appropriate cations is rather limited, therefore one may try to use a pair of different cations instead. The present study demonstrates that even two cations with fairly different size may randomly accommodate interstices between the vanadium-oxygen layers. This approach seems to be very promising for the search of new layered vanadium oxides since combinations of two different cations provide an easy way to adjust the cation size and modify the spin system in a controlled manner.

In conclusion, we prepared and investigated the complex vanadium oxide \(Pb_{0.55}Cd_{0.45}V_2O_5\). Its crystal structure is similar to that of \(CaV_2O_5\). The new compound reveals a system of weakly antiferromagnetically coupled dimers with an intradimer interaction of about 270 K. In our approach using microscopic model with averaged hopping parameters we were able to describe the influence of structural changes on the magnetic interactions. Nearest-neighbor exchange interactions in the \([V_2O_5]\) layers are decreased with the increase of the interatomic distances from \(CaV_2O_5\) to \(Pb_{0.55}Cd_{0.45}V_2O_5\) while the type of spin system remains unchanged.

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### TABLE IV: Comparison of nearest-neighbor exchange interactions and geometrical parameters for \(MV_2O_5\) compounds

| Compound          | \(J_1\) (K) | \(d(V–V)\) (Å) | \(\angle VO(3)V\) (deg) | \(J_2\) (K) | \(d(V–V)\) (Å) | \(\angle VO(2)V\) (deg) |
|-------------------|-------------|----------------|-------------------------|-------------|----------------|-------------------------|
| \(Pb_{0.55}Cd_{0.45}V_2O_5\) | 303         | 3.550(5)       | 132.1(3)                | 26          | 3.667(7)       | 137.3(2)                |
| \(CaV_2O_5\)      | 608\*       | 3.493\*        | 132.9\*                 | 122\*       | 3.604\*        | 135.3\*                 |
| \(MgV_2O_5\)      | 92\*        | 3.372\*        | 117.6\*                 | 144\*       | 3.692\*        | 141.1\*                 |

\(\text{Ref. } 12\)
\(\text{Ref. } 15\)
\(\text{Ref. } 16\)
B. Normand, K. Penc, M. Albrecht, and F. Mila, Phys. Rev. B 56, R5736 (1997); cond-mat/9703214.

V. Petřiček, M. Dušek, and L. Palatinus, Jana2000. The crystallographic computing system (2000), Institute of Physics, Praha, Czech Republic.

K. Koepernik and H. Eschrig, Phys. Rev. B 59, 1743 (1999).

J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).

H. Eschrig, Optimized LCAO Method and the Electronic Structure of Extended Systems (Springer, Berlin, 1989).

Anisotropic broadening was observed for weak (0k0) reflections. It may be caused by slight inhomogeneities in the Pb/Cd distribution over the crystallites.

V. Ivanshin, V. Yushankhai, J. Sichelschmidt, D. Zacharov, E. Kaul, and C. Geibel, Phys. Rev. B 68, 064404 (2003).

The weight error due to the presence of the amorphous phase in the samples under investigation may be revealed by fitting high-temperature susceptibility data with Curie-Weiss law and analyzing the value of the effective magnetic moment. We use the data in the temperature range of 350 – 400 K and find reasonable fitting parameters ($\mu_{\text{eff}} = 1.51 \mu_B$, $\Theta = -110$ K) that support our conclusions. The spin-only value of $\mu_{\text{eff}}$ for V$^{+4}$ is 1.73 $\mu_B$, while the experimental value is 13% lower consistent with the decrease of $g$. 

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