Magnetic properties of PdAs$_2$O$_6$: a dilute spin system with an unusually high Néel temperature

M. Reehuis, T. Saha-Dasgupta, D. Orosel, J. Nuss, B. Rahaman, B. Keimer, O. K. Andersen, and M. Jansen

1Helmholtz-Zentrum Berlin für Materialien und Energie, D-14109 Berlin, Germany
2S. N. Bose National Center for Basic Sciences, Salt Lake, Kolkata 700098, India
3Max Planck Institute for Solid State Research, D-70569 Stuttgart, Germany

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The crystal structure and magnetic ordering pattern of PdAs$_2$O$_6$ were investigated by neutron powder diffraction. While the magnetic structure of PdAs$_2$O$_6$ is identical to the one of its isostructural 3d-homologue NiAs$_2$O$_6$, its Néel temperature (140 K) is much higher than the one of NiAs$_2$O$_6$ (30 K). This is surprising in view of the long distance and indirect exchange path between the magnetic Pd$^{2+}$ ions. Density functional calculations yield insight into the electronic structure and the geometry of the exchange-bond network of both PdAs$_2$O$_6$ and NiAs$_2$O$_6$, and provide a semi-quantitative explanation of the large amplitude difference between their primary exchange interaction parameters.

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I. INTRODUCTION

The magnetic properties of transition metal compounds with 3d valence electrons have been one of the central research themes in solid-state physics for the past three decades. In view of the interplay between magnetism and high-temperature superconductivity, particular attention has been focused on oxides and arsenides. Recently, the electronic structure and ordering phenomena of transition metal compounds with 4d and 5d valence electrons (such as ruthenates and iridates) have also captured much attention. The electronic correlations in these materials are generally weaker than those of their 3d counterparts, while the spin-orbit coupling is stronger. The quantitative description of the influence of these parameters on the electronic phase behavior of d-electron compounds is an important topic of current research. Here we report a detailed investigation of the magnetic properties of PdAs$_2$O$_6$, a recently synthesized electrically insulating compound with a magnetic lattice of Pd$^{2+}$ ions in the electron configuration 4d$^8$. We compare our results to the isostructural compound NiAs$_2$O$_6$, which is based on Ni$^{2+}$ ions with the same number of electrons in the 3d-shell.

PdAs$_2$O$_6$ crystallizes in the PbSb$_2$O$_6$ structure with Pd$^{2+}$ and As$^{5+}$ ions segregated into different layers (Fig. 1). The octahedral coordination of Pd$^{2+}$ in this structure is unusual, because divalent palladium shows a strong preference for square-planar coordination, which is associated with a diamagnetic ground state. Only a few examples of sixfold-coordinated Pd$^{2+}$ compounds are known, including the ambient- and high-pressure polymorphs of PdF$_2$ as well as fluoro-palladates of composition MPdF$_4$ (M = Ca, Cd, Hg) and CsPdF$_4$. Two of these compounds are paramagnetic at high temperatures and tend to order antiferromagnetically upon cooling. In accord with this trend, magnetic susceptibility measurements on PdAs$_2$O$_6$ showed paramagnetic behavior at room temperature, and an antiferromagnetic phase transition at the Néel temperature $T_N \sim 150$ K. This behavior is qualitatively analogous to the one of the isostructural 3d-homologues MnAs$_2$O$_6$, CoAs$_2$O$_6$, and NiAs$_2$O$_6$, which also show antiferromagnetic ordering with $T_N = 13$, 20, and 30 K, respectively. However, the much higher Néel temperature of PdAs$_2$O$_6$ is surprising, especially because the Pd$_6$-octahedra do not share vertices, edges or faces. The exchange paths connecting neighboring Pd$^{2+}$ ions are therefore long and involve at least two bridging oxygen sites.

In order to elucidate the microscopic origin of this surprising behavior, we have used neutron diffraction to determine the magnetic structure of PdAs$_2$O$_6$, which turned out to be identical to that of the 3d-homologues (Section II). This implies similar networks of exchange bonds in both sets of compounds. We employed density-functional calculations to obtain insights into the electronic structure of PdAs$_2$O$_6$ and NiAs$_2$O$_6$, and specifically into the origin of the exchange paths (which turned out to be hopping via As dimers) and of the large amplitude difference of the primary exchange interaction parameters (Section III). A model based on these interactions yields an excellent description of the magnetic susceptibilities of both compounds.

II. NEUTRON DIFFRACTION

A. Experimental details

A powder sample of PdAs$_2$O$_6$ of weight $\sim 3$ g was prepared using the starting materials PdO (99.9 % metals basis, Alfa Aesar) and As$_2$O$_3$ (99.9 %, Alfa Aesar) in the molecular ratio 1 : 1.1 as described earlier. The mixed powder was pressed into pellets and dried in evacuated silica tubes for 12 h at 373 K. Then the evacuated silica tubes were heated up to 973 K with a rate of 100 K/h. The hygroscopic and air sensitive powder of PdAs$_2$O$_6$ was obtained after an annealing process of about 100 hours. Measurements of the magnetic susceptibility and specific heat were carried out in the temperature range between 5 and 300 K (Fig. 2). Both quantities show anomalies indicative of antiferromagnetic ordering of the Pd sublattice at 140 K, in agreement with prior work.

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the crystal and magnetic structure were carried out with the program FullProf. We used the nuclear scattering lengths \( b(\text{Pd}) = 5.91 \text{ fm} \), \( b(\text{As}) = 6.58 \text{ fm} \) and \( b(\text{O}) = 5.805 \text{ fm} \). The magnetic form factors of the magnetic ions were taken from Ref. 6.

B. Crystal structure of PdAs\(_2\)O\(_6\)

The crystal structure of PdAs\(_2\)O\(_6\) was recently refined from x-ray powder diffraction data in the trigonal PbSb\(_2\)O\(_6\)-type structure (space group \( \text{P}3\text{1m}, \text{No.} \ 162 \)), where the Pd, As and O atoms are in the Wyckoff positions \( 1a(0,0,0) \), \( 2d(\frac{1}{3}, \frac{2}{3}, \frac{1}{3}) \) and \( 6k(x,0,z) \), respectively. The same space group was found earlier for the compounds MnAs\(_2\)O\(_6\), CoAs\(_2\)O\(_6\) and NiAs\(_2\)O\(_6\) containing 3d-metal ions. From our neutron powder diffraction data taken at the lower temperatures 5 and 200 K (Fig. 3) the trigonal space group \( \text{P}3\text{1m} \) was confirmed. For the Rietveld refinements we used data in the extended \( 2\theta \) range from \( 4^\circ \) up to \( 146^\circ \). A total of 14 parameters was refined: an overall scale factor, five profile function parameters, the zero point, two lattice constants, the positional parameters \( x \) and \( z \) of the oxygen atom as well as three isotropic thermal parameters. The powder sample contained small amounts of the binary oxide PdO, which crystallizes in the tetragonal space group \( \text{P}4_2/mmc \). Therefore the overall scale factor of PdO was additionally allowed to vary during the refinements.

In Table I the results of the refinements are compared with those of the x-ray study carried out earlier at room temperature. Here it can be seen that the positional parameters of the oxygen atoms determined at 5 and 200 K are in good agreement, indicating that the structural changes between the magnetically ordered and the paramagnetic states are weak. Only a slight reduction of 0.0036 Å (about 6 \( \sigma \)) could be observed for the Pd-O-bond length in the PdO\(_6\)-octahedra. In contrast, the distances between the As and O-atoms are practically unchanged (Table I). The value \( d(\text{As-O}) = 1.8281(6) \text{ Å} \) (at 200 K) found for PdAs\(_2\)O\(_6\) is in very good agreement with the values of other arsenates containing 3d-metal ions: \( d(\text{As-O}) = 1.827(4) \text{ Å} \) (NiAs\(_2\)O\(_6\)), \( d(\text{As-O}) = 1.830(3) \text{ Å} \) (CoAs\(_2\)O\(_6\)), \( d(\text{As-O}) = 1.826(2) \text{ Å} \) (MnAs\(_2\)O\(_6\)), and \( d(\text{As-O}) = 1.826(1) \text{ Å} \) (CdAs\(_2\)O\(_6\)). All of these values are in agreement with \( d(\text{As-O}) = 1.82 \text{ Å} \) calculated for an AsO\(_6\)-octahedron given by Shannon. In Table I it can be seen that the structural parameters obtained at 200 and 300 K show relatively large discrepancies despite the fact that both data sets were collected in the paramagnetic phase. This can be ascribed to the larger scattering power of the O-atoms in neutron diffraction, with the consequence that the O-positions can be determined more reliably. Furthermore, the shortest oxygen contact \( d(\text{O-O}) = 2.308(3) \text{ Å} \) was found to be implausibly short in the x-ray study. From our neutron diffraction study we found the larger values \( d(\text{O-O}) = 2.3757(12) \text{ Å} \) at 5 K and \( d(\text{O-O}) = 2.3726(12) \text{ Å} \) at 200 K, respectively. The value \( d(\text{O-O}) = 2.410(3) \text{ Å} \) found for NiAs\(_2\)O\(_6\) is slightly larger, while the

![Fig. 1: (Color online) Crystal structure of AAs\(_2\)O\(_6\) (A = Pd, Ni) showing the three-dimensional network of AO\(_6\) and AsO\(_6\) octahedra. The brown (dark grey) colored balls denote A atoms, and the cyan (light grey) colored balls represent As atoms. Small black colored balls at the corners of the octahedra are O atoms.](image1)

![Fig. 2: Temperature dependence of the specific heat and the inverse magnetic susceptibility of PdAs\(_2\)O\(_6\).](image2)
The presence of the strong magnetic reflection (0, 0, 1/2)_M indicates that the magnetic moments of the Pd-atoms are aligned ferromagnetically within the hexagonal ab-plane. Due to antiferromagnetic exchange interactions between the palladium moments the ferromagnetic layers form the sequence + - + along the c-axis (Fig. 4). With this model the magnetic structure of PdAs_2O_6 could be successfully refined using the magnetic reflections observed in the 2θ-range up to 50°. It has to be noted that the moment direction within the hexagonal plane cannot be determined from the refinements. The wave vector k = (0, 0, 1/2) keeps the full symmetry of the group G_6 = G according to magnetic group theory, and it defines the magnetic translation lattice. The existence of three magnetic domains in the hexagonal basis plane prohibits an unambiguous determination of the moment direction.

In order to improve the refinement of the magnetic structure, we used the purely magnetic intensities obtained from the difference between the data sets collected at 5 and 200 K (inset of Fig. 3). Since the magnetic form factor of Pd^{2+} is not available, we first used the one of the Pd^{2+}ion, but Table II shows that the calculated intensities decrease much more strongly with increasing 2θ than the observed ones. A considerably better fit was obtained with the form factor of Ni^{2+}, which also shows a d^{8}-configuration. The relatively large residual R_M = 0.141 [defined as R_M = \sum |I_{obs} - I_{calc}|/|I_{obs}|] reflects the fact that the low intensities of the magnetic reflections at high 2θ-values could not be measured with good accuracy, in combination with systematic errors arising from the difference between the form factors of Pd^{2+} and Ni^{2+}.

As-O-bond lengths d(As-O) = 1.827(4) Å (NiAs_2O_6) and d(As-O) = 1.8281(6) Å (PdAs_2O_6) are practically the same in both compounds. The cell volume of the Ni compound (V = 86.97(3) Å^3) is much smaller than the one of the Pd compound (V = 93.698(2) Å^3). This is due to fact that the ionic radius of Pd^{2+} is larger than that of Ni^{2+}. In order to keep the As-O-bond lengths almost constant in the AsO_6-octahedra, the bond angle ∠(O-As-O) increases from 169.91(3)° in PdAs_2O_6 to 173.23(12)° in NiAs_2O_6.

C. Magnetic structure of PdAs_2O_6

The neutron powder data recorded at 5 K show additional Bragg reflections that can be ascribed to the antiferromagnetic order of the Pd sublattice. The two prominent ones at 2θ = 9.5° and 2θ = 23.5° can be indexed as (0, 0, 1/2)_M and (0, 1, 1/2)_M, respectively. This suggests that the magnetic cell has a doubled c-axis with a propagation vector k = (0, 0, 1/2). All further magnetic reflections were assigned indices according to (hkt)_M = (hkt)_N ± k, where M and N designate the magnetic and nuclear reflections. The same type of magnetic ordering was observed earlier for the isotypic divalent transition metal arsenates CoAs_2O_6 and NiAs_2O_6. The existence of three magnetic domains in the hexagonal basis plane prohibits an unambiguous determination of the moment direction.

In order to improve the refinement of the magnetic structure, we used the purely magnetic intensities obtained from the difference between the data sets collected at 5 and 200 K (inset of Fig. 3). Since the magnetic form factor of Pd^{2+} is not available, we first used the one of the Pd^{2+}ion, but Table II shows that the calculated intensities decrease much more strongly with increasing 2θ than the observed ones. A considerably better fit was obtained with the form factor of Ni^{2+}, which also shows a d^{8}-configuration. The relatively large residual R_M = 0.141 [defined as R_M = \sum |I_{obs} - I_{calc}|/|I_{obs}|] reflects the fact that the low intensities of the magnetic reflections at high 2θ-values could not be measured with good accuracy, in combination with systematic errors arising from the difference between the form factors of Pd^{2+} and Ni^{2+}.
| $T$ [K] | 5 K | 200 K | 290 K |
|--------|-----|-------|------|
| a [Å]  | 4.81700(4) | 4.81837(5) | 4.8196(1) |
| c [Å]  | 4.65618(6) | 4.66014(7) | 4.6646(1) |
| V [Å³] | 93.565(2) | 93.698(2) | 93.835(3) |
| $x$(O) | 0.37187(15) | 0.37230(16) | 0.3695(7) |
| $z$(O) | 0.28203(18) | 0.28236(18) | 0.2926(5) |
| $B$(Pd) [Å$^2$] | 0.46(3) | 0.62(3) | 0.80(3) |
| $B$(As) [Å$^2$] | 0.49(2) | 0.54(2) | 0.88(3) |
| $B$(O) [Å$^2$] | 0.62(2) | 0.74(2) | 0.55(6) |
| $d$(Pd-O) [Å] | 2.22116(6) (6×) | 2.22476(6) (6×) | 2.24372(20) (6×) |
| $\angle$(O-Pd-O) [°] | 180 (3×) | 180 (3×) | 180 (3×) |
| $d$(As-O) [Å] | 1.8288(6) (6×) | 1.82811(6) (6×) | 1.8076(23) (6×) |
| $\angle$(As-O) [°] | 169.913(3) (3×) | 169.793(3) (3×) | 170.42(13) (3×) |
| $d$(O-O)$_{\text{min}}$ [Å] | 2.3757(12) | 2.3726(12) | 2.308(3) |
| $R_p$ | 0.0241 | 0.0298 | 0.0859$^*$ |

Table I: Results of Rietveld refinements of the neutron powder diffraction data ($\lambda = 1.5476$ Å) for the nuclear structure of PdAs$_2$O$_6$ at 5 and 200 K. The lattice constants, positional and isotropic thermal parameters as well as the bond distances and angles within the AsO$_6$- and PdO$_6$-units are compared with the values obtained earlier at room temperature from x-ray powder diffraction data ($\lambda = 0.7093$ Å). The residual $R_p$ of the refinement of the crystal structure is defined as $R_p = \sum ||F_{\text{obs}}|| - ||F_{\text{calc}}||/||F_{\text{obs}}||$. The residual for the room temperature structure (marked by $^*$) was calculated with intensities rather than structure factors.$^1$

The sublattice magnetization resulting from the refinement is $\mu = 1.92(4)\mu_B$ per Pd site, similar to the value $\mu = 2.11(3)\mu_B$ reported for NiAs$_2$O$_6$ (Ref.3). While the ordered moment is consistent with the spin-only moment expected for a $d^8$ configuration, a fit to the magnetic susceptibility for $T > T_N$ yields a g-factor larger than 2, which is indicative of an orbital contribution to the Pd moment (see Section III.C below). The difference may in part be due to zero-point fluctuations of the magnetic moment, which reduce the ordered moment of the spin-1 system in the binary oxide NiO by $\sim 8\%$. The zero-point reduction is possibly larger in PdAs$_2$O$_6$ because of the low-dimensional exchange-bond network (see Section III.C). While these considerations suggest a small but nonzero orbital contribution to the Pd moment, measurements of the g-factor anisotropy by single-crystal neutron diffraction and/or electron spin resonance will be required to quantify this contribution.

![Fig. 4: (Color online) Magnetic structure of PdAs$_2$O$_6$. Shown are the isolated PdO$_6$-octahedra between the AsO$_6$-layers. The magnetic moments of the palladium atoms are aligned ferromagnetically within the hexagonal ab-plane. Along the c-direction the moments are coupled in an antiparallel fashion, forming the sequence + · + ·.](image)

### III. DENSITY FUNCTIONAL CALCULATIONS

#### A. LDA band structure

Figure 5 shows the electronic band structure and density of states in the paramagnetic local density-functional approximation (LDA)$^{12}$ for NiAs$_2$O$_6$ in solid lines and for PdAs$_2$O$_6$ in dashed lines. The self-consistent calculations were performed with the linear muffin-tin orbital (LMTO) method$^{13}$ using $8 \times 8 \times 8$ k-points in the Brillouin zone.

The Fermi level falls in the middle of the two narrow transition-metal (A) $e_g$-bands. These are split above the three narrow $t_{2g}$-bands, because the $pd\sigma$-hopping is $\sim \sqrt{3}$ times stronger than the $pd\pi$-hopping to the O $p$ orbitals at the corners of the AO$_6$-octahedron. This is in accord with the labeling $A^{2+}$. Similarly, in accord with the labeling $O^{2-}$ and $As^{5+}$, the oxygen $2p$-like bands are below and the As $s$-and As $p$-like bands are above the Fermi level. However, in

| $I_{\text{obs}}$ | $I_{\text{calc}}$ (Ni$^{2+}$) | $I_{\text{calc}}$ (Pd$^+$) | $\theta$(°) |
|--------------|-----------------|-----------------|---------|
| (0, 0, $\frac{1}{2}$)$_M$ | 518 | 445 | 503 | 9.5 |
| (1, 0, $\frac{1}{2}$)$_M$ | 198 | 205 | 178 | 23.5 |
| (2, 0, $\frac{1}{2}$)$_M$ | 9 | 34 | 25 | 28.8 |
| (0, 1, $\frac{1}{2}$)$_M$ | 88 | 87 | 50 | 36.2 |
| (1, 1, $\frac{1}{2}$)$_M$ | 42 | 45 | 23 | 38.8 |
| (1, 1, $\frac{1}{2}$)$_M$ | 43 | 28 | 11 | 44.8 |
| (0, 2, $\frac{1}{2}$)$_M$ | 2 | 6 | 2 | 49.1 |

Table II: Observed and calculated intensities of the magnetic reflections of PdAs$_2$O$_6$ as obtained from Rietveld refinements using the magnetic form factors of Ni$^{2+}$ and Pd$^+$. The residual $R_M$ is defined as $R_M = \sum ||I_{\text{obs}}|| - ||I_{\text{calc}}||/||I_{\text{obs}}||$.  

The Fermi level falls in the middle of the two narrow transition-metal (A) $e_g$-bands. These are split above the three narrow $t_{2g}$-bands, because the $pd\sigma$-hopping is $\sim \sqrt{3}$ times stronger than the $pd\pi$-hopping to the O $p$ orbitals at the corners of the AO$_6$-octahedron. This is in accord with the labeling $A^{2+}$. Similarly, in accord with the labeling O$^{2-}$ and As$^{5+}$, the oxygen $2p$-like bands are below and the As $s$- and As $p$-like bands are above the Fermi level. However, in
terms of atomically localized orbitals (LMTOs) rather than
Wannier orbitals, the bands denoted as As in the figure
have ~40% anti-bonding O p character, as well as some As
and O s characters. Correspondingly, around -12 eV (below
the frame of the figure) there are two bands with As s
and O sp bonding characters in about equal amounts.

With the bands lined up at the Fermi level, the t_{2g}
and p bands lie lower in the Pd than in the Ni compound.
This is because 4d orbitals have a larger extent and therefore
larger hopping integrals to O p than do 3d orbitals. For the
same reason, the e_{g} band is about 1.4 times wider in the Pd
than in the Ni compound.

Inclusion of the Coulomb interaction beyond the LDA
splits the e_g bands and leads to insulating solutions, as
we have checked through LDA + U calculations. For the
present purpose of calculating and understanding the mag-
netic properties, it is more convenient to start from the
localized description and treat the hopping, t, to order
t^2/U.

B. Pd e_g Wannier orbitals, low-energy tight-binding
Hamiltonian and magnetic interactions

We therefore construct a low-energy Hubbard Hamilton-
ian. Since the LDA e_g band is narrow and well sepa-
rated from all other bands, we can limit the one-electron
Hilbert space to that of the two A-centered Wannier orbi-
tals, 3z^2-r^2 and x^2-y^2, describing this band. When
using the NMTO downfolding method, we thus kept the
A e_g degrees of freedom as active, and downfolded the
rest. The Wannier orbitals are finally obtained by sym-
metrically orthonormalizing the downfolded, Nth-order
muffin-tin orbitals (NMTOs).

In the representation, \( H = \sum_{\nu_{im},j\nu'} \chi_{\nu_{im},j\nu'} + h.c. \), of the corresponding one-electron
part of the Hamiltonian, \( \chi_{\nu_{im},j\nu'} \) is the hopping integral from
orbital \( m \) on site \( i \) to orbital \( m' \) on site \( j \).

Figure 6 shows the \( x^2 - y^2 \) and \( 3z^2 - r^2 \) Wannier orbitals
for PdAsO_6 as \( \chi (r) = \pm const. \) surfaces with positive lobes
colored red and negative blue. The z-axis points along the
Pd-O bond in the bc-plane and the x- and y-axes point to the
other oxygens in the Pd-centered octahedron. In the figure,
the latter has been given a blue, transparent skin while all
As-centered octahedra have been given a red, transparent
skin. Pd atoms are green, As atoms yellow, and oxygens
violet. Such a Pd-centered Wannier orbital has \( x^2 - y^2 \)
or \( 3z^2 - r^2 \) character locally, and strong pdr antibonding
character on the neighboring oxygens. The unusual feature
here is that the back-lobes of the strongest O p characters
(the four \( p_x \) and \( p_y \) tails of the \( x^2 - y^2 \) Wannier orbital and
the two \( p_z \) tails of the \( 3z^2 - r^2 \) Wannier orbital) bond to the
sp characters on the closest pair of As atoms and, from there,
antibond to the closest oxygen, which now belongs to
a neighboring PdO_{6} octahedron. As an example: The
red lobe of the \( x^2 - y^2 \) orbital sticking up and out towards
the reader, antibonds with the blue lobe of near \( p_z \) orbital,
whose red back-lobe merges together (bonds) with the red,
two-center As sp bond, giving rise to a “red sausage”. The
latter finally antibonds with the O p orbital which points
upwards towards a near Pd belonging to the upper Pd-sheet
(not shown in the figure). Similarly for the \( 3z^2 - r^2 \) orbital
on the right-hand side of the figure: Its red lobe, sticking
down and out, antibonds with the blue lobe of the near \( p_z \)
orbitals, which merges with the As two-center bond into a red
sausage. The latter finally induces strong p\_g-like character
which points down and out, towards a Pd atom in the lower
Pd sheet.

These hopping paths, shown schematically in Fig. 7,
are to 3rd-nearest Pd neighbors, but only to six out of the
twelve, namely to those at \( \pm (0, 1, 1) \), \( \pm (\sqrt{3}, 1, 2, 1) \),
and \( \pm (\sqrt{3}, 0, 1, 1) \). The e_g integrals for hopping to the
3rd-nearest neighbors at \( \pm (0, 1, -1) \), \( \pm (\sqrt{3}, 1, 2, 1) \), and
\( \pm (\sqrt{3}, 0, 1, 1) \), which have no bridging oxygen and As pairs,
are negligible. The calculated hopping integrals exceeding
10 meV are given in Table III. We see that those to 3rd-
nearest neighbors dominate those to 2nd- and 1st-nearest
neighbors.
Fig. 6: (Color online) The $x^2 - y^2$ (left panel) and $3z^2 - r^2$ (right panel) Wannier orbitals which span the LDA Pd $e_g$ bands of PdAs$_2$O$_6$. Plotted are orbital shapes (constant-amplitude surfaces) with lobes of opposite signs colored red (dark) and blue (light). For clarity, the central PdO$_6$ octahedron is given a blue skin and all AsO$_6$ octahedra a red skin. Pd atoms are green, As atoms yellow, and oxygens violet.

Fig. 7: (Color online) Paths of the dominant hoppings. Dashed green: between $x^2 - y^2$ orbitals (see left-hand side of Fig. 6) on 3rd-nearest A neighbors. Solid red: between $3z^2 - r^2$ orbitals (see right-hand side of Fig. 6) on 3rd-nearest A neighbors. The colors of the atoms are as in Fig. 1.

The Ni 3$d$ ($e_g$) Wannier orbitals in NiAs$_2$O$_6$ are similar to the Pd 4$d$ ($e_g$) Wannier orbitals in PdAs$_2$O$_6$, except that they are more localized. This is consistent with the 1.4 times smaller 3$d$ ($e_g$)-band width. Concomitantly, the hopping integrals for NiAs$_2$O$_6$ listed in parentheses in Table III are about 1.4 times larger than those for PdAs$_2$O$_6$.

The magnetic exchange interaction, $J$, can be expressed in general as a sum of antiferromagnetic and ferromagnetic contributions. In the limit of large Coulomb correlation, typically valid for late transition metal elements like Pd or Ni, the antiferromagnetic contribution is related to the hopping integral $t$ by the second-order perturbation relation $J \sim \frac{t^2}{U}$, where $U$ is the effective on-site Coulomb repulsion defined for the Wannier orbitals. Considering the hopping integrals in Table III, the contribution from the $t^2$ term in the magnetic exchange gives rise to a factor two difference between the Pd and Ni compounds. The estimate of $U$, unlike that of the hopping integral $t$, is a rather delicate issue. In principle, one should compute $U$ for the Wannier orbitals shown in Figure 7. However lacking a prescription to do so, we computed the $U$ values corresponding to Ni-$d$ and Pd-$d$ partial waves, which were truncated outside the atomic spheres defined around an Ni or Pd sites. The calculations were carried out within the framework of the constrained DFT scheme. The $U$ values calculated in this way were $U_{Ni} = 8.4$ eV and $U_{Pd} = 5.7$ eV. But since the Wannier $e_g$ orbitals are far more delocalized than the truncated partial waves, and more so for Pd than for Ni, these $U$ values should be significantly reduced, and more so for Pd than for Ni. This could conceivably lead to the factor $U_{Ni}/U_{Pd} \sim 2.4$ needed to bring our theoretical $t^2/U$ estimate for the Néel temperatures of the two compounds into agreement with the measured ratio of 4.7.

C. Spin model and susceptibility

Taking into account only the dominant hopping integrals provided by the NMTO-downfolding calculation, a spin model can be defined in terms of the six pairs of 3rd-nearest-neighbor magnetic interactions, all of size $J_3$, obtained by
Table III: Hopping integrals between Wannier \( e_g \) orbitals centered on Pd (or Ni). Hoppings are in meV and listed are those exceeding 10 meV. Only hoppings between 2nd-nearest neighbors, \( d_2 = 4.82 \) (4.76) Å, and between 3rd-nearest neighbors, \( d_3 = 6.71 \) (6.51) Å, are significant.

| Vector from \( m \) to \( m' \rightarrow \) | \(+ (0,1,0)\) | \(+ \left( \frac{\sqrt{2}}{2}, \frac{1}{2}, 0 \right)\) | \(+ \left( \frac{\sqrt{2}}{2}, -\frac{1}{2}, 0 \right)\) | \(+ (0,1,1)\) | \(+ \left( \frac{\sqrt{2}}{2}, \frac{1}{2}, -1 \right)\) | \(+ \left( \frac{\sqrt{2}}{2}, -\frac{1}{2}, -1 \right)\) |
|---|---|---|---|---|---|---|
| \( 3z^2 - r^2, 3z^2 - r^2 \) | 33 (24) | .( ) | .( ) | -139 (-99) | -38 (-27) | -38 (-27) |
| \( x^2 - y^2, x^2 - y^2 \) | -12 (-12) | 22 (15) | 22 (15) | .( ) | -106 (-76) | -106 (-76) |
| \( 3z^2 - r^2, x^2 - y^2 \) | .( ) | -19 (-16) | 19 (16) | .( ) | 58 (42) | -58 (-42) |

This model was solved by the quantum Monte Carlo method\(^{19}\) on a \( 10 \times 10 \times 10 \) lattice. The primary interaction \( J_3 \), and the effective Landé \( g \)-factors were obtained by fitting to the experimental susceptibility. As shown in Fig. 8, the calculated and measured susceptibilities agree very well. The optimal values of the \( g \)-factor and the exchange parameter \( J_3 \), were found to be respectively 2.38 and 62 K for the Pd compound, and 2.48 and 13 K for the Ni compound. We find that the \( g \)-factors are larger than the spin-only value of 2, in accord with the discussion in Section II.C above. The fit of the susceptibilities yields a value of 5 for the ratio of the predominant magnetic exchange parameters of PdAs\(_2\)O\(_6\) and NiAs\(_2\)O\(_6\), in good agreement with the ratio of the magnetic transition temperatures.

Fig. 8: (Color online) Temperature dependence of the magnetic susceptibility (multiplied by temperature) for NiAs\(_2\)O\(_6\) (left panel) and PdAs\(_2\)O\(_6\) (right panel). The circles correspond to experimental data (taken from Ref.3 for NiAs\(_2\)O\(_6\)), and the solid lines correspond to calculated data based on the model described in the text.

IV. CONCLUSIONS

Using a combination of susceptibility and neutron diffraction measurements, we have developed a comprehensive experimental description of the magnetic properties of the newly synthesized antiferromagnet PdAs\(_2\)O\(_6\). Density functional theory has provided a detailed understanding of the magnetic bond network of this compound, as well as a semiquantitative explanation of the large enhancement of the magnitude of its primary exchange interaction parameters compared to its 3d homologue NiAs\(_2\)O\(_6\). This approach may prove useful for research on other Pd compounds including the recently discovered\(^{20}\) ferromagnet PdS\(_2\)O\(_7\), and for comparative studies of materials with 4d valence electrons and their 3d-electron counterparts in general.

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\(^{7}\) Present address: Aliah University, DN-41, Sector-V, Salt Lake, Kolkata 700091, India

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