Investigation of Low-Dimensional Vanadium-Oxide Spin-Systems

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Reducing the dimensionality in solids can lead to unusual magnetic and/or electrical properties which have attracted considerable attention in the past years. In magnetic systems, these unusual properties are largely due to quantum effects of the spins. Thus, one expects to observe them especially in systems with a low spin $\boldsymbol{S} = 1/2$ or $\boldsymbol{S} = 1$. The $\boldsymbol{S} = 1/2$ systems based on Cu^{2+} (one hole in the ***d***-shell) have very extensively been studied after the discovery of high temperature superconductivity. Their electron counterparts, i.e., systems based on Ti^{3+} or V^{4+} with one electron in the ***d***-shell, have been much less investigated. Therefore, our oxide project, which is conducted in cooperation with the group of Prof. Antipov at the Moscow State University, was focused on the search and investigation of new low-dimensional complex oxides based on V^{4+}, V^{3+} or Ti^{3+} showing unusual magnetic or electrical properties**.**

$Sr_2V_3O_9$ and $Ba_2V_3O_9$: Quasi one-dimensional $S = 1/2$ systems

Our first subject was the synthesis and investigation of the low-dimensional compounds $Sr_2V_3O_9$ and $Ba_2V_3O_9$ (since these compounds contain one V^{4+}- and two V^{5+}-ions they can also be written as $\boldsymbol{A}_2VO(VO_4)_2$). Although these compounds and their crystal structure have already been known for a few years [1-4] almost no information on their physical properties were available. We synthesized polycrystalline samples of both compounds and investigated their magnetic properties by means of susceptibility, magnetization, specific heat, optical, Raman, ESR and NMR measurements [5, 6]. Preliminary results were already presented in the previous report [7]. The detailed data we have now collected show that both compounds are quasi one-dimensional spin systems. An unusual upturn in the low temperature susceptibility was initially attributed to a sizeable Dzyaloshinsky-Moriya- (DM-) interaction. Furthermore, both our magnetic and structural investigations point to an interesting structural instability related to the displacement of the V^{4+}-ion out of the center of the VO_6 octahedra, leading to the formation of one short vanadyl V-O bond. Measurements of the dielectric properties, however, did not give evidence for ferro- or antiferroelectric transitions [8]. These results have prompted theoretical calculation: For $Ba_2V_3O_9$ we have estimated the contribution of the DM-interaction with a quantum-chemical calculation using a realistic structure of vanadium 3***d***- and oxygen 2***p***-orbitals. We have found that this effect is far too small to explain the experimental results. Instead, numerical investigations of small clusters using the finite-temperature Lanczos method suggest that the Curie upturn is due to a segmentation of spin chains caused by broken magnetic bonds between adjacent VO_6-octahedra [9]. This segmentation is related to the instability of the orientation of the vanadyl bond. In contrast the anisotropy of the susceptibility and the ESR results support the relevance of the DM-interaction in $Sr_2V_3O_9$. Meanwhile, we have grown single crystals and are investigating the problem of the DM-interaction and of the ordering of the vanadyl bond in more detail.

$Pb_2VO(PO_4)_2$: The second example for a frustrated square lattice

By homovalent substitution of Sr by Pb and of the two V^{5+}-ions by P^{5+} in $\boldsymbol{A}_2VO(VO_4)_2$, we recently discovered a new compound with very interesting magnetic properties: $Pb_2VO(PO_4)_2$. The crysral structure of this compound which was solved by R.V. Shpanchenko and A.V. Mironov at the Moscow State University is completely different from that of the previous investigated $\boldsymbol{A}_2V_3O_9$ compounds (Fig. 1). It is composed of layers of two interpenetrating lattices of VO_5 pyramids connected by one common PO_4 tetrahedron. These layers are separated by large P_2O_7 groups and Pb atoms, resulting in a quite large distance between these

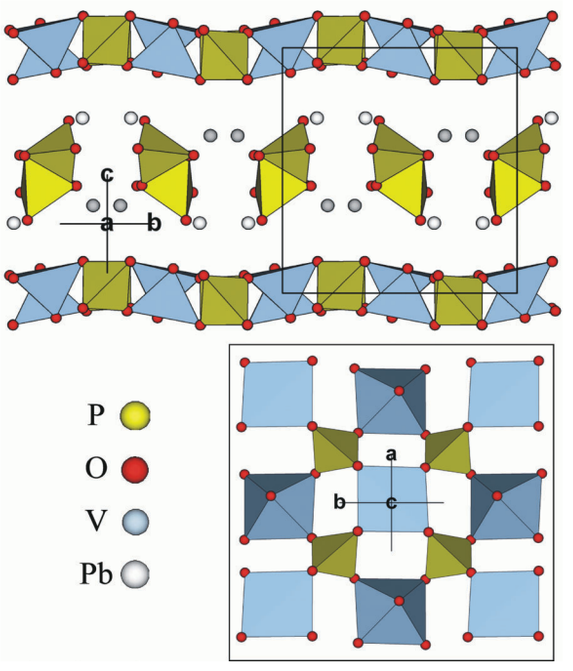

Fig. 1: View of the crystal structure of $Pb_2VO(PO_4)_2$. Lower part: view of the layer with the up and down pointing VO_5 pyramids connected by PO_4 tetrahedra.

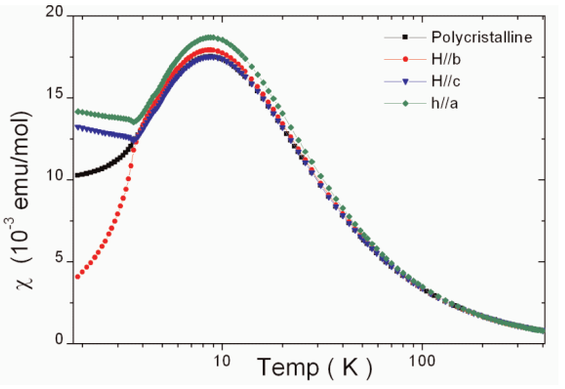

Fig. 2: Temperature dependence of the susceptibility of $Pb_2VO(PO_4)_2$ polycrystals as well as of single crystals along different directions.

layers and thus in a very strong two-dimensional character. Within a layer, all VO_5 pyramids pointing to the same direction (up or down) form an almost square lattice, the middle of the square being occupied by a pyramid pointing to the opposite direction. On the basis of basic rules for superexchange, one expects a weak magnetic interaction $\boldsymbol{J}_1$ between nearest V-neighbors (one V being in an up and one in a down pyramid) while the superexchange $\boldsymbol{J}_2$ between next nearest V-neighbors (which are both either in up or down pyramids) should be stronger.

This exchange topology corresponds to a frustrated square lattice. Frustrated square lattices have been the subject of intensive theoretical calculation some years ago, because one expects an interesting magnetic phase diagram as a function of the ratio $\boldsymbol{J}_1/\boldsymbol{J}_2$. However no experimental data were available for comparison because no experimental realization of such an exchange topology was known. Only recently, a first example, Li_2VOSiO_4, has been discovered [10]. The topology of the layers in Li_2VOSiO_4 is almost identical to that in $Pb_2VO(PO_4)_2$, but the separation between the layers is much smaller, leading to a sizeable interlayer exchange. Thus, we expect our new compound to be the second example for a frustrated square lattice with a much stronger two-dimensional character than the first example.

Meanwhile, we have synthesized both polycrystals and single crystals and performed detailed susceptibility $\chi(\boldsymbol{T})$ and specific heat $\boldsymbol{C}(\boldsymbol{T})$ measurements. The results confirm that $Pb_2VO(PO_4)_2$ is a frustrated square lattice system. $\chi(\boldsymbol{T})$ (Fig.2) follows at high temperatures a Curie-Weiss law with an effective moment μ_{eff} = 1.70 μ_B close to the expected spin-only-value for V^{4+}. The Curie-Weiss temperature θ = 4 K gives an estimate for the sum of $\boldsymbol{J}_1$ and $\boldsymbol{J}_2$. The broad maximum observed in $\chi(\boldsymbol{T})$ at $\boldsymbol{T}_{\chi max}$ = 8.2 K is a hallmark for low dimensional spin system and corresponds to the onset of antiferromagnetic correlations. At $\boldsymbol{T}_N$ = 3.6 K, a kink in $\chi(\boldsymbol{T})$ marks the transition to an ordered state which we suspect to be the collinear antiferromagnetic structure expected for $\boldsymbol{J}_2 > \boldsymbol{J}_1$. Below $\boldsymbol{T}_N$ the anisotropy in the susceptibility indicates that in the ordered state the moments are aligned along the ***b***-axis. These properties are quite similar to those of Li_2VOSiO_4. In our compound, the characteristic temperatures $\boldsymbol{T}_{\chi max}$ and $\boldsymbol{T}_N$ are slightly larger, whereas θ is slightly lower. The ratio $T_N/\boldsymbol{T}_{\chi max}$ is smaller indicating a stronger frustration or/and a smaller ratio between interlayer and in-layer coupling in $Pb_2VO(PO_4)_2$.

The specific heat data (Fig. 3) show only a very small anomaly at $\boldsymbol{T}_N$ in zero external field. However, this anomaly increases very strongly upon increasing the field to a few Tesla. This is expected for a low dimensional quantum spin system. At low fields, only a very small part of the magnetic entropy is released at the magnetic order-

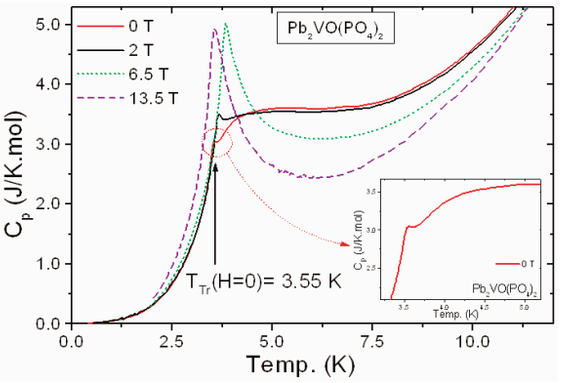

Fig. 3: Temperature dependence of the specific heat of $Pb_2VO(PO_4)_2$ polycrystals for different applied magnetic fields. Inset: Anomaly at T_N for B = 0 T.

ing. Most of the entropy is released at higher temperatures where the antiferromagnetic correlations disappear. Applying a magnetic field introduces a further anisotropy which suppresses quantum fluctuations and thus leads to a transfer of the entropy release from the high temperature region to the magnetic ordering region, as observed in our data. Our $C(T)$ data above T_N compare quite well with theoretical results for a simple square lattice calculated by G. Uhrig at the university of Cologne. This comparison suggests that the frustration is not too strong. A deeper analysis of $\chi(T)$ and C(T) in cooperation with N. Shannon and K. Penc from the theory group of the neighboring PKS-Institute suggests a weak ferromagnetic J_1, the main evidence being a large $T_{\chi max}/\theta$ ratio. $Pb_2VO(PO_4)_2$ would then be the first example of a new kind of frustrated system which has not yet been investigated, neither theoretically nor experimentally.

In summary, we have discovered a new interesting two-dimensional complex vanadium oxide, $Pb_2VO(PO_4)_2$. The results of our susceptibility and specific heat measurements indicate that it is the second example for a frustrated square lattice system. Even more interestingly, these results suggest the nearest neighbor exchange to be ferromagnetic, which would result in a new kind of frustrated system. In the next future, we plan to analyze our data more deeply using new theoretical results for the susceptibility and specific heat of a frustrated square lattice system. Further on, we hope to be able to perform NMR and Neutron scattering experiments in order to determine the antiferromagnetic structure and the strength of the magnetic exchange.

References

[1] ***J. Feldmann and Hk. Müller-Buschbaum,*** Z. Naturforsch. **50b**, 43-46 (1995).

[2] ***J. Feldmann and Hk. Müller-Buschbaum,*** Z. Naturforsch. **51b**, 489- 492 (1996).

[3] ***A.-C. Dhaussy, F. Abraham, O. Mentre and H. Steinfink,*** J. Solid State Chem. **126**, 328-335 (1996).

[4] ***O. Mentre, A.-C. Dhaussy, F. Abraham and H. Steinfink.*** J. Solid State Chem. **140**, 417-427 (1998).

[5] ***E.E. Kaul, H. Rosner, V. Yushankhai, J. Sichelschmidt, R.V. Shpanchenko and C. Geibel,*** submitted to Phys. Rev. B ; Cond-Mat 0209409.

[6] ***A.A. Gippius, E.N. Morozowa, D.F. Khozeev, R.V. Shpanchenko, E.E. Kaul, C. Geibel, A. Rabis, M. Baenitz and F. Steglich,*** submitted to Phys. C.

[7] ***C. Geibel, M. Baenitz, M. Dischner, E.E. Kaul, E. Morré, R. Mischalak, J. Sichelschmidt, G. Sparn, F. Steglich and M. Weiden,*** Development of the Institute and Scientific Report, ***"Quasi-one-dimensional soin-system in 3d-compounds"***, 136-141 (2000).

[8] ***V. Bobnar, P. Lunkenheimer, A. Loidl, E.E. Kaul and C. Geibel.*** Solid State Comm. **122**, 595-599 (2002).

[9] ***B. Schmidt, V. Yushankhai, L. Siurakshina and P. Thalmeier,*** cond-mat/0210204.

[10] ***P. Melzi, P. Carretta, A. Lascialfari, M. Mambrini, M. Troyer, P. Millet and F. Milla,*** Phys. Rev. Lett. **85**, 1318-1321 (2000); ***Melzi P., S. Aldrovandi, F. Tedoldi, P. Carretta, P. Millet and F. Milla.*** Phys. Rev. B **64**, 024409 1-10 (2001).

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