

**MAGNETIC STUDY OF PARAMAGNETIC COMPOUNDS
M(AsF₆)₂ (M = Co, Mn) AND Co(AsF₆)₂·2L (L = AsF₃, SbF₃, SO₂)**

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† This paper is dedicated to the memory of Dr. Karel Lutar

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Abstract

DC magnetization measurements with a SQUID susceptometer have been performed on Mn(AsF₆)₂, Co(AsF₆)₂ and three Co(AsF₆)₂ compounds with different ligands (AsF₃, SbF₃, SO₂). All samples demonstrate paramagnetic behavior above 50 K. The measured Curie constants are compatible with Mn⁺² and Co⁺² ions. In addition, the samples with Co atoms show magnetic ordering below 40 K.

Investigation of arsenic NQR only in Co(AsF₆)₂·2AsF₃ reveals three lines: one near 122 MHz and two near 50 MHz. Relation of these spectral lines to the structure is obtained. Possible influence of paramagnetic Co is examined.

Introduction

M(AsF₆)₂ (M = transition metal) and M(AsF₆)₂·2L (L = AsF₃, SbF₃, SO₂, etc.) type of compounds can be used as starting materials for the preparation of new binary fluorides of transition metals in high oxidation states.^{1,2} For effective use of these compounds profound research of their physical and chemical properties is advantageous. Applying the spectroscopic method of nuclear quadrupole resonance (NQR), a quadrupole nucleus present in the sample (e.g. ⁷⁵As) offers one possible view of the structural and paramagnetic properties of these materials. However, this method proved to be fruitful only in one investigated compound so far (Co(AsF₆)₂·2AsF₃).³ Because of excessive paramagnetic broadening of the NQR spectra in the other compounds, we turned to the magnetization measurements. We expanded our preliminary DC magnetization measurements using a home made SQUID with the measurements on the

commercial SQUID magnetometer (Quantum Design MPMS-XL-5). Temperature or field dependence of the magnetization in these compounds depends to a great extent on the bonding orbitals of the unpaired paramagnetic electrons, which is an interesting feature, connected with the crystal structure. The magnetic study of the compounds $M(\text{AsF}_6)_2$ ($M = \text{Co}, \text{Mn}$) and their complexes $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$, $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{SbF}_3$ and $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{SO}_2$ is the main subject of this article. The compounds have been synthesized at the Department of Inorganic Chemistry and Technology at J. Stefan Institute (Slovenia) as described in the literature.^{1,2} Due to their reactivity they must be handled and preserved in very dry inert atmosphere (argon).

In this family of compounds the following two crystal structures, shown schematically in Figures 1 a, c and 2 a, c were published: $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ ¹ and $\text{Mn}(\text{AsF}_6)_2$.² On the basis of X-ray powder diffraction data we reasonably expect for the third compound $\text{Co}(\text{AsF}_6)_2$ to be isostructural to $\text{Mn}(\text{SbF}_6)_2$.⁴ The schematic structure is shown in Figures 1 b and 2 b. We assume that the complexes with the ligands SbF_3 and SO_2 show structural similarities with $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$.

The discussed cobalt compounds obviously tend to form layered structures, like the ones in Figures 2 a, b. AsF_6 octahedra connect two or three Co ions across the fluorine bridges. Two (Figure 1 a) or three (Figure 1 b) of the six fluorines in the octahedron are engaged for this job, leaving terminal status to the remaining fluorines. Each Co ion (most probable ground state $3d^7 \ ^4F_{9/2}$) is surrounded by six fluorines belonging to six AsF_6 anions (Figures 2 a, b; cf. also the structures $\text{H}_3\text{OM}(\text{AsF}_6)_3$ ($M = \text{Mn}, \text{Co}, \text{Ni}$),⁵ not included in the present magnetic measurements). The Co ions, mutually interconnected by the AsF_6 groups, form parallel layers, separated by layers of AsF_6 groups or different ligand layers.

$\text{Mn}(\text{AsF}_6)_2$ has essentially a different structure.² Each Mn ion (most probable ground state $3d^5 \ ^6S_{5/2}$) is here surrounded not by 6 but by 8 fluorines. An important reason for the increased coordination might be the ionic diameter which is in Mn^{2+} 10% larger than in Co^{2+} ion. Four equatorial fluorines around Mn belong to four different AsF_6 groups approximately in the same plane, whereas two fluorine pairs on upper and lower side belong to two AsF_6 octahedra approaching their edges to both Mn poles. On the other hand, in each AsF_6 octahedron four fluorines are engaged in chemical bonds to

Mn: two opposite octahedral apices point to two neighboring Mn ions in Mn-F-As-F-Mn chain. Two proximate fluorines of the remaining four share the third Mn atom while the other two F keep terminal positions (see Figure 1 c). The crystal structure thus consists of a rectangular network of double chains -Mn-F-As-F-Mn-F- running in the directions x and y. In the z direction these chains are connected by double fluorine bridges $\text{As}=\text{F}_2=\text{Mn}=\text{F}_2=\text{As}$, as shown in Figure 2 c.

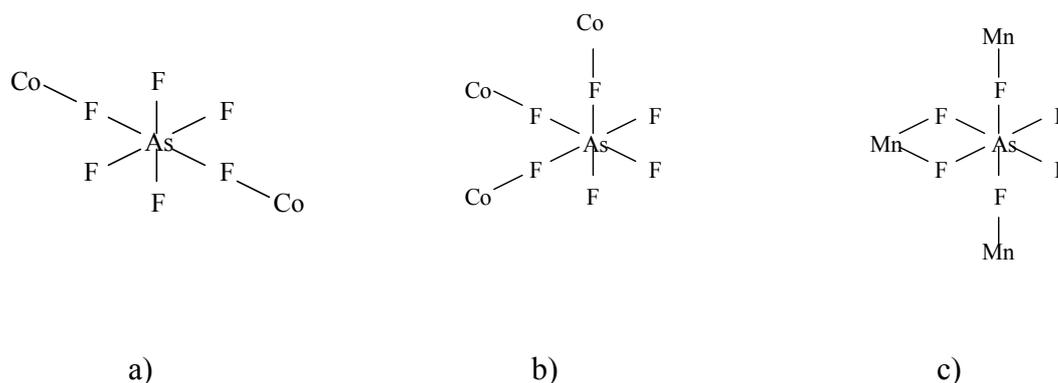


Figure 1. Coordination of crystal lattice constituents AsF_6 to the paramagnetic ions (schematic) a) in $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$, b) in $\text{Co}(\text{AsF}_6)_2$, c) in $\text{Mn}(\text{AsF}_6)_2$.

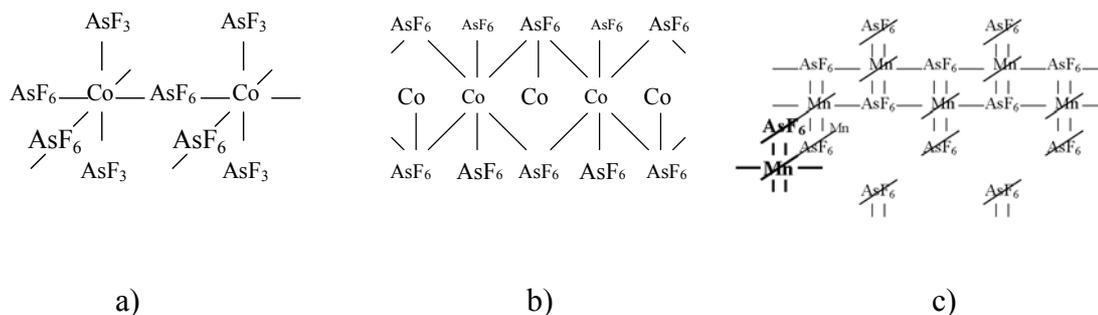


Figure 2. Schematic crystal structures: a) $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ (layers); b) $\text{Co}(\text{AsF}_6)_2$ (layers); c) $\text{Mn}(\text{AsF}_6)_2$ (crossed chains; vertical lines || represent bonding between Mn and As over two proximate F atoms from the same AsF_6 group). The 3rd dimension (out of/into the page) is indicated by increased/decreased character size.

Arsenic NQR

Measuring the temperature dependence of ^{75}As NQR spectra, the arsenic nuclei in these compounds can serve as natural probes of the local electric and magnetic fields as well as an indicator of the lattice dynamics. Superregenerative NQR spectrometer has detected three resonances in $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$. At 298 K the lower two are located at 49.5 and 52.7 MHz with nearly linear temperature dependence and relatively small positive temperature coefficient about 2 kHz/K down to 180 K. There both lines disappear in noise. They belong to the two types of As atoms in two AsF_6 octahedra, slightly different from each other. The high frequency line (122.1 MHz at 298 K, negative temperature coefficient -60 kHz/K), which should belong to the AsF_3 pyramid, seems to exhibit Bayer like $\nu(T)$ behavior and it reaches 129.5 MHz at 77 K.³

Pulse measurements of the two low frequency NQR lines show extremely short relaxation times; below 0.05 ms. At lower temperature the relaxation doesn't slow down appreciably, however the signal gradually disappears. This behavior is very likely due to the efficient relaxation centers - paramagnetic Co^{+2} ions. Their broadening influence on the As NQR line is probably partly averaged out by the superexchange coupling between the paramagnetic nuclei (Co-F-As-F-Co) and consequent fast magnetic fluctuations.^{6,7}

In the related compounds $\text{Co}(\text{AsF}_6)_2$, $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{SbF}_3$, $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{SO}_2$ and $\text{Mn}(\text{AsF}_6)_2$ arsenic NQR signals seem to be broadened beyond detectability by paramagnetic local fields. In two of these materials with known structures, $\text{Co}(\text{AsF}_6)_2$ and $\text{Mn}(\text{AsF}_6)_2$, the superexchange coupling of the paramagnetic ions differs from $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ in an increased number of Co or Mn atoms coupled to the observed one. As seen in Figure 2, in the previous case this number was four, whereas in $\text{Co}(\text{AsF}_6)_2$ case it is twelve (equal couplings: Co-F-As-F-Co) and in $\text{Mn}(\text{AsF}_6)_2$ eight (four Mn-F-As-F-Mn and four Mn=F2=As-F-Mn). Moreover, in the latter superexchange couplings sharper veering of the bond chain can be noticed. All these features probably slow down the paramagnetic fluctuations and smear out the arsenic NQR signals. As mentioned before, arsenic NQR was not observable in the other two $\text{Co}(\text{AsF}_6)_2$ complexes either, although we suppose there similar situation as in $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$.

Magnetization measurements

DC magnetization measurements have been performed in a SQUID magnetometer (Quantum Design MPMS-XL-5). Magnetization was measured as a function of temperature in the magnetic field strength $H = 1000$ Oe from room temperature down to 2 K. This magnetic field strength is small enough that the induced magnetization is still far from the saturated value regardless the temperature. The susceptibility $\chi(T) = M/H$ was obtained from the measured data.

Magnetization versus magnetic field strength $M(H)$ was measured at 2 K and at 50 K from $H = 0$ to $\pm 50\,000$ Oe which is the highest reachable magnetic field strength for the used SQUID magnetometer.

In $\text{Mn}(\text{AsF}_6)_2$ (Figure 3) susceptibility follows the Curie-Weiss law $\chi = C/(T-\theta)$ over the whole measured temperature range (300 K - 2 K) with $C = 3.9$ emu K/mol Oe and $\theta = -2$ K. The Curie constant is close to the expected value^{8,9} for Mn^{+2} ions. Magnetization versus magnetic field strength $M(H)$ at 2 K shows no hysteresis and can be described by the Brillouin function with saturated magnetization equal to $4.1 \mu_B$ per molecule $\text{Mn}(\text{AsF}_6)_2$.

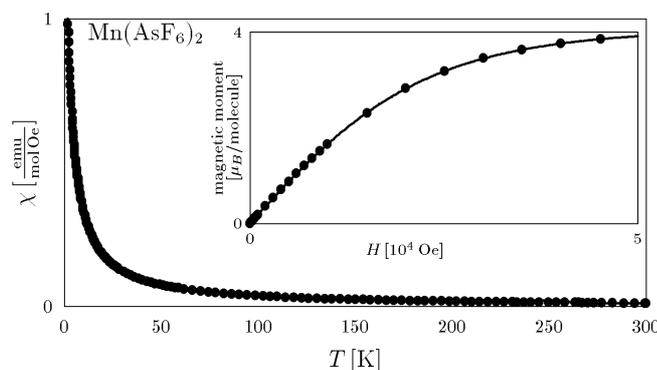


Figure 3. $\chi(T)$ in $\text{Mn}(\text{AsF}_6)_2$. Full line represents Curie-Weiss law $\chi=C/(T-\theta)$ with $C = 3.9$ emu K/mol Oe and $\theta = -2$ K. The inset represents magnetic moment per molecule $\text{Mn}(\text{AsF}_6)_2$ versus H . The full line is the Brillouin function with the saturation $4.1 \mu_B$ per molecule.

Susceptibility in all four samples with Co ions follows the Curie-Weiss law from room temperature to approximately 40 K. This temperature region of the susceptibility can be well described by average Curie constant $C = (2.7 \pm 0.1)$ emu K/mol Oe, the typical value given for Co^{+2} ions^{8,9}. Three values of the θ parameter (see Table 1), obtained by fitting procedure in the Curie-Weiss region, are absolutely somewhat larger and fall into the negative region, which is characteristic for antiferromagnets.⁸

When cooling the Co samples below 40 K the susceptibility increases much more than it is predicted by the Curie-Weiss law and probably a magnetic phase transition occurs at those temperatures. Insets on the graphs on Figures 4 show the differences in magnetization between the measured susceptibility and the calculated one with $C = 2.7$ emu K/mol Oe.

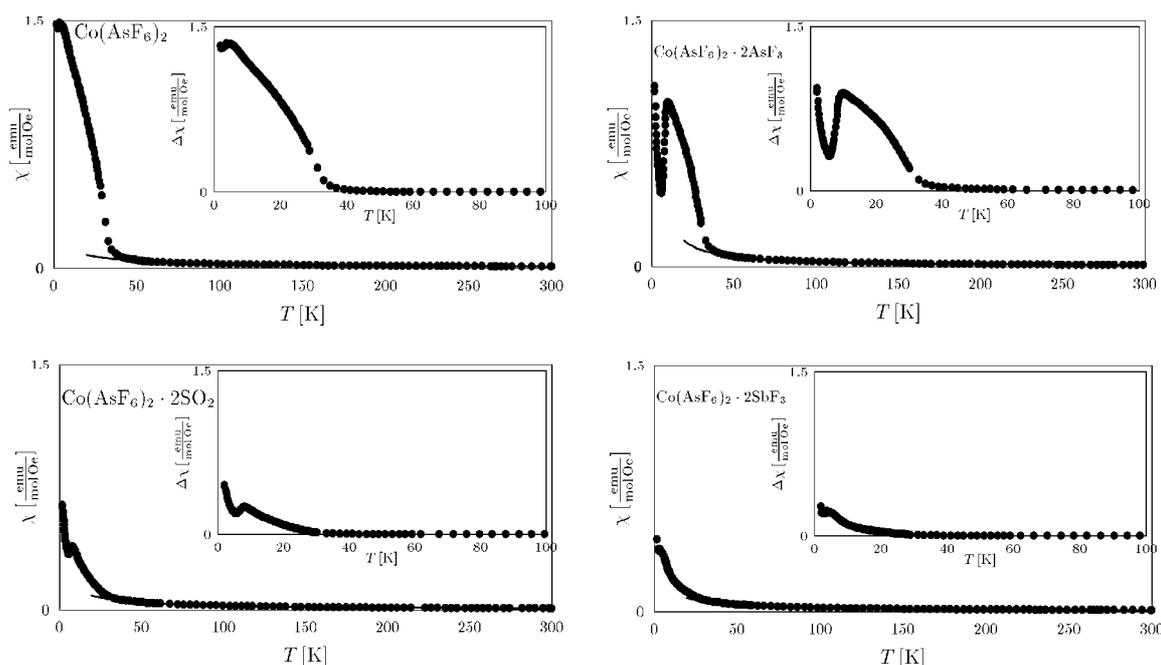
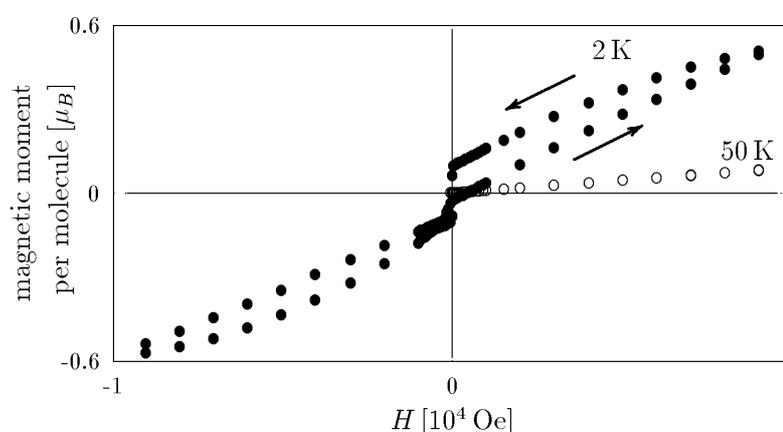


Figure 4. $\chi(T)$ in $\text{Co}(\text{AsF}_6)_2$, $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$, $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{SO}_2$ and $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{SbF}_3$. Full lines represent Curie-Weiss law $\chi = C/(T-\theta)$ with C and θ chosen to minimize difference between the measured $\chi(T)$ with the calculated one in the temperature interval 50 K to room temperature. Insets in all four figures represent differences in magnetization between the measured data and the calculated susceptibility from the Curie-Weiss law with the parameters C and θ obtained from the measured data for $T > 50$ K.

Table 1. The fitting parameters C and θ from the Curie-Weiss law.

| | C [emu K/mol Oe] | θ [K] |
|---|--------------------|--------------|
| $\text{Mn}(\text{AsF}_6)_2$ | 3.9 | -2 |
| $\text{Co}(\text{AsF}_6)_2$ | 3.0 | -18 |
| $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ | 2.9 | 2 |
| $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{SO}_2$ | 2.8 | -13 |
| $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{SbF}_3$ | 2.7 | -14 |

Figure 5. The average magnetic moment per molecule in $\text{Co}(\text{AsF}_6)_2$ at 2 K and at 50 K.

The presence of a hysteresis at 2 K suggests the occurrence of a spin canting¹⁰ at these temperatures. Therefore the compound can be classified as a weak ferromagnet.

Discussion and Conclusions

The arsenic NQR measurements show the absence of observable, sharp lines in all the samples except in $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$. This reflects the strong line narrowing in the $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ case by fast paramagnetic fluctuations due to proper superexchange coupling between Co ions. In the other samples the fluctuations may be slower because of higher multiplicity of the coupling and because of sharper veering of chemical bonds (weaker superexchange).

SQUID measurements of the dc magnetization in five different $\text{M}(\text{AsF}_6)_2$ ($\text{M} = \text{Co}, \text{Mn}$) compounds reveal paramagnetic behavior above 40 K in all samples. The measured

Curie constants in Co and Mn compounds imply that the Co^{2+} and Mn^{2+} ions prevail in these compounds.

The increase of susceptibility in the four samples containing Co^{+2} ions below 40 K indicates magnetic transitions. The low value of the magnetization at 50 kOe below the transition (note also hysteresis at 2 K, Figure 5) and the smooth and linear increase of it indicate that the compounds present an antiferromagnetic ordering with some spin canting which prevents total compensation of the magnetic moment of the samples. While above 40 K (paramagnetic region) the susceptibilities of all the Co samples are similar, the susceptibilities in the ordered phases deviate from compound to compound. Of course, they depend much more on the detailed superexchange pathways.

The Mn compound stays paramagnetic down to 2 K. Such a difference between the two kinds of materials remains to be explained. Maybe the layered structure, which favors antiferromagnetism and spin canting by the cobalt samples, or the unusual Mn coordination or chained structure of $\text{Mn}(\text{AsF}_6)_2$ are at the origin of such a difference.

References and Notes

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Povzetek

S pomočjo susceptometra na osnovi SQUIDA smo opravili meritve dc magnetizacije v $\text{Mn}(\text{AsF}_6)_2$ in v štirih spojinah $\text{Co}(\text{AsF}_6)_2$ z različnimi ligandi. Vsi vzorci se nad 50 K obnašajo paramagnetno. Izmerjene Curiejeve konstante ustrezajo ionom Mn^{+2} in Co^{+2} . Vzorci s Co atomi izkazujejo poleg pretežnega paramagnetnega obnašanja pod 40 K tudi znake magnetnega urejanja.

Meritev JKR arzena je samo v $\text{Co}(\text{AsF}_6)_2 \cdot 2\text{AsF}_3$ odkrila tri črte: eno v bližini 122 MHz in dve v bližini 50 MHz. Proučili smo zvezo tega spektra s kristalno strukturo in vpliv paramagnetnega Co.