Heat capacity, magnetic and lattice dynamic properties of pseudo-two dimensional: M$_2$Fe$_2$O(AsO$_4$)$_2$ [M=K, K$_{0.79}$Cs$_{0.21}$ and Rb] compounds

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ABSTRACT

In this paper, structural, magnetic and heat capacity of M$_2$Fe$_2$O(AsO$_4$)$_2$ compounds have been reported. Most interestingly, the magnetization at very low fields a complete negative magnetization was observed in both field cooling and zero field cooling in K$_2$Fe$_2$O(AsO$_4$)$_2$ and Rb$_2$Fe$_2$O(AsO$_4$)$_2$ compounds whereas field cooled is positive in KCsFe$_2$O(AsO$_4$)$_2$. A possible mechanism for the observed peculiar magnetic behavior is discussed, related to the competition of the single ion magnetic anisotropy and the antisymmetric magnetization behavior in two crystallographically different FeO$_6$ centers. We estimated the gap (Δ) opening at low temperature K$_2$Fe$_2$O (AsO$_4$)$_2$; KCsFe$_2$O (AsO$_4$)$_2$ and Rb$_2$Fe$_2$O (AsO$_4$)$_2$, are 23.6 K, 23.9 K and 25 K respectively from heat capacity. Magnetic part of heat capacity at low temperatures follows the T$^3$ dependence, indicates that the low temperature magnetic state in all these compounds are antiferromagnetic. Copyright © 2016 VBRI Press.

Keywords: Magnetization; heat capacity; magnetic frustrations: antiferromagnetic.

Introduction

Magnetic frustration is a consequence of a system’s inability to minimize the energy of all near-neighbor (NN) interactions at the same time due to the geometric arrangement of magnetic moments in the lattice [1]. As a result, many frustrated magnetic systems have multiple degenerate ground state configurations, which make them susceptible to spin fluctuations. Magnetically frustrated systems do not typically exhibit conventional long-range order, and instead have a strong propensity to remain dynamic. In cases where long-range order does develop, often times it does not occur until very low temperatures and exotic ordering patterns of the magnetic moments are observed. There has been significant experimental and theoretical work on triangular and pyrochlore magnetic systems and the effects of frustration on the ordering and fluctuations. A recent topic of interest is on systems where the triangles or tetrahedra are broken into isolated units, a recent example is Cu$_3$TeO$_4$Cl$_3$ [2]. Also steps magnetization has been observed in molecular magnets and a few condensed solids like Dy$_2$Ti$_2$O$_7$ and Ho$_2$Ti$_2$O$_7$ and Ca$_3$Co$_2$O$_6$ [3, 4]. These characteristic may be ascribed to geometrical circumvent magnetic structures [5] or ions with uniaxial magnetic properties [6] or spin rearrangements or domain wall depinning [7]. Also the observation of negative magnetization (NM) has become more interesting phenomena can be effectively utilized for various device applications such as various magnetic memories, thermo magnetic switches and magnetic cooling/heating devices [8]. Recently, Sundaresan et al. have explored the NM in CoCr$_2$O$_4$ under zero field cooled mode is arising from the trapped magnetic field and same nature has been observed in CoFe$_2$O$_4$, CoFeCrO$_4$ and its derivatives compounds [9-11]. In fact, it was shown earlier that even earth’s magnetic field can influence the magnetization behavior of certain magnetic materials. However, LaSrCoRuO$_6$ [12, 13] and orthovanadate RVO$_3$ compounds (R=La, Nd, Sm, Gd, Er, and Y) [14] are two of most widely studies systems that shows negative magnetization during ZFC and FC in very low applied fields. In LaSrCoRuO$_6$ the NM in the low magnetic field ZFC is due to Ru to Ru via oxygen atom ferromagnetic interactions which polarize the paramagnetic Co spins in a direction opposite to applied field giving rise to magnetic compensation [15]. For such an effect to be observed, inequivalent sites must exist [16]. However, Goodenough and Nguyen suggested that the response of the orbital moment to the forces generated at the first-order phase transition can reverse the Dzyaloshinsky vector of an antisymmetric interaction so as to create a canted spin component in a direction opposite to the applied field, given that particular temperature which is close to $T_v$ [17].

In the scope of exploring new materials featuring magnetic nanostructures, we have been investigating transition metal containing silicate, phosphate, and arsenate compounds with dimension-dependent magnetic properties.
The magnetic nanostructures in question are made of transition-metal-oxide (TM-oxide) lattices that are structurally isolated by oxynions (SiO₄²⁻, PO₄³⁻, AsO₄³⁻) and, through sharing common oxygen atoms, linked into three-dimensional framework structures. Because of the closed-shell, nonmagnetic nature of the Si²⁺, P³⁺ and As⁵⁺ ions, the magnetic interactions are confined as evidenced by magnetic anomalies not seen in the corresponding bulk TM-oxide lattices [18-21]. Furthermore, these compounds are magnetic insulators exhibiting periodic arrays of magnetic nanostructures due to crystallinity. During the last decade, the TM containing silicate, phosphate, and arsenate have been intensively investigated in order to get insight into the underlying physical mechanisms and to search for new candidates with intriguing properties [20].

M₂Fe₂O₅(AsO₄)₂ [M=K, and Rb] are a pseudo-two-dimensional iron(III) arsenates compounds previously reported by Lii et al [21]. A high yield of crystals was obtained using molten halide flux techniques. We have observed a complete negative magnetization for both ZFC and FC in very low applied field in K and Rb compounds and crossover of the ZFC magnetization from negative to positive at relatively higher field below their magnetic ordering temperature. To our knowledge there is no any research reports are available on de
tices that are

Results and discussion

Fig. 1 shows the Rietveld refined pattern of the room temperature x-ray diffractograms of M₂Fe₂O₅(AsO₄)₂ compounds with M= K, Rb. The refinement reveals that all the compounds are single phase and crystallize in orthorhombic structure (Space group Pnma, No. 62) [21].

The lattice parameters obtained from refinement of these compounds are given in Fig. 2a. It may be noted from figure that the lattice parameter increases as M changes from K to Rb. This variation is attributed to increase in the ionic radii of the M⁺ ions. Pivoting on the oxo-oxyn, Fe₂O₄₀ and FeO lattice is body forming a wavy wire of FeO₆. Each Fe atom is connected to the other Fe atoms via µ₂-oxo bridging modes within the Fe−O−As slabs. The chain of FeO₆ octahedra are separated from 7.826 Å (minimum distance between Fe−Fe between Fe−O−As slabs) which suggests that magnetic interactions between them are comparatively weak and the dominant magnetic exchange is between Fe²⁺ ions within the Fe−O chains. Within the extended wires FeO₆ octahedra are connected by sharing common vertex with variation in distance between Fe(2)−Fe(2) from 2.8788(6)−2.8946(6) Å in K to Rb compounds (Fig. 2b) whereas almost unchanged in distance between Fe(1)−Fe(2) 3.076(3) Å. Both types Fe−Fe distances are shorter than those between the vertex-sharing polyhedra (3.38−3.88 Å). However, Fe−Fe distances are too large for significant direct magnetic exchange to occur too. The Fe-O-Fe angles through the µ₁ oxo oxygen are 89.80(2) ° and 105.90(2) ° are less than those through the shared vertices. Given the diversity of bond distances and angles, multiple super exchange pathways and, thus, complex magnetic interactions are expected [21, 22].
Fig. 2. (a) Lattice parameters and (b) distances of Fe$_2$-Fe$_2$ atoms of M$_2$Fe$_2$O(AsO$_4$)$_2$.

Fig. 3 a-c shows the temperature dependence of magnetic susceptibility for M$_2$Fe$_2$O(AsO$_4$)$_2$ compounds in temperature range of 2-300 K in an applied field of 1000 Oe. We have calculated the ordering temperature (T$_{ord}$) using the dM/dT vs T plots. We observed T$_{ord}$ = 25 K, 21 K and 24 K in K$_2$Fe$_2$O(AsO$_4$)$_2$, KCs$_2$Fe$_2$O(AsO$_4$)$_2$ and Rb$_2$Fe$_2$O(AsO$_4$)$_2$ respectively. The least square fit of temperature range 70-300 K data to the Curie-Weiss equation, \( \chi = C/(T - \theta_C) \), where \( C \) is the Curie constant, and \( \theta_C \) is the Weiss constant, yielded the best-fit values of \( C \) = 19.96, 17.32 and 9.26 emu·K/mol for K$_2$Fe$_2$O(AsO$_4$)$_2$, KCs$_2$Fe$_2$O(AsO$_4$)$_2$ and Rb$_2$Fe$_2$O(AsO$_4$)$_2$ respectively whereas \( \theta_C \) = -1162.5 K, -788.5 and -510 K. The observed effective moment per Fe$^{3+}$ atom (shown in Table 1) are larger than expected calculated value of 5.9 μB. The large and negative Weiss constant shows the strong antiferromagnetic (AFM) interaction.

Table 1. Lattice parameters \( a, b \) & \( c \), ordering temperature (T$_{ord}$), magnetization (M) at H= 30 kOe, effective moment (\( \mu_{eff} \)) and the paramagnetic Curie temperature (\( \theta_C \)) in M$_2$Fe$_2$O(AsO$_4$)$_2$ compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( a ) (Å)</th>
<th>( b ) (Å)</th>
<th>( c ) (Å)</th>
<th>T$_{ord}$ (K)</th>
<th>M$_s$ (( \mu_B )/f.u.)/Fe$^{3+}$</th>
<th>( \mu_{eff} ) (( \mu_B ))/Fe$^{3+}$</th>
<th>( \theta_C ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$Fe$_2$O(AsO$_4$)$_2$</td>
<td>8.5369(2)</td>
<td>5.7577(1)</td>
<td>17.935(4)</td>
<td>25</td>
<td>0.1683</td>
<td>8.97</td>
<td>-1162.5(9.2)</td>
</tr>
<tr>
<td>CsK$_2$Fe$_2$O(AsO$_4$)$_2$</td>
<td>8.5504(2)</td>
<td>5.7631(1)</td>
<td>18.211(4)</td>
<td>21</td>
<td>0.3039</td>
<td>8.36</td>
<td>-788.5(3.2)</td>
</tr>
<tr>
<td>Rb$_2$Fe$_2$O(AsO$_4$)$_2$</td>
<td>8.5331(2)</td>
<td>5.7892(2)</td>
<td>18.611(4)</td>
<td>24</td>
<td>0.2312</td>
<td>6.54</td>
<td>-510(6.5)</td>
</tr>
</tbody>
</table>

Zero field cooling (ZFC) and Field cooling (FC) measurements of the magnetic moment were also carried out on M$_2$Fe$_2$O(AsO$_4$)$_2$ in the form of ground single crystals and aligned single crystals in different fields within a small temperature range between 2–30 K.

Fig. 3. Temperature dependent magnetic DC susceptibility of (a) K$_2$Fe$_2$O(AsO$_4$)$_2$; (b) KCs$_2$Fe$_2$O(AsO$_4$)$_2$ and (c) Rb$_2$Fe$_2$O(AsO$_4$)$_2$. Solid red line is fitted with Curie-Weiss law’s.

Fig. 4 shows the FC and ZFC of the aligned single crystals in different applied field. The magnetization of the FC and ZFC largely depend on the applied magnetic field. At very low applied field ~10 Oe in aligned single crystals, it is completely negative in K$_2$Fe$_2$O(AsO$_4$)$_2$ and Rb$_2$Fe$_2$O(AsO$_4$)$_2$ whereas ZFC is negative and FC is positive in KCs$_2$Fe$_2$O(AsO$_4$)$_2$. Such type reversal effect in M-T data is occurring, due strong magnetic anisotropy a partial cancellation of antiferro-magnetically coupled magnetic sublattice (In our system Fe$^{3+}$ occupies two
nonequivalent sites) with different magnetic moments [15]. During the FC process, the sample is cooled in the presence of a magnetic field.

![Image](https://via.placeholder.com/150)

**Fig. 4.** Temperature dependent magnetization of $\text{K}_2\text{Fe}_2\text{O}(\text{AsO}_4)_2$ (a&b), and $\text{Rb}_2\text{Fe}_2\text{O}(\text{AsO}_4)_2$ (c&d) under ZFC and FC mode in different field. Normalize magnetization data of $\text{KC}_3\text{Fe}_2\text{O}(\text{AsO}_4)_2$ (c&d) under ZFC and FC mode in different field.

Therefore, the spins will be locked in a particular direction depending on the strength of the applied field, as soon as the system is cooled below its ordering temperature. The FC magnetization will remain almost constant if the anisotropy of the sample is very low or increase with decreasing temperature by showing a ferro or ferrimagnetic transition. This kind of behavior can be observed in a well-studied system, RVO$_3$ compounds (R=La, Nd, Sm, Gd, Er, and Y) [16]. In ZFC magnetization increases rapidly from paramagnetic region to a ferromagnetic region below the blocking temperature ~30 K and it reaches a maximum $T_{\text{max}}$ ~ 22, 19 and 23 K in $\text{K}_2\text{Fe}_2\text{O}(\text{AsO}_4)_2$, $\text{KC}_3\text{Fe}_2\text{O}(\text{AsO}_4)_2$ and $\text{Rb}_2\text{Fe}_2\text{O}(\text{AsO}_4)_2$ respectively and after that decreases monotonously. It crosses zero at $T \sim 21$ K and becomes negative by achieving a minimum. With further decrease in temperature, the magnetization remains negative but it achieves very close to zero magnetization. This kind of behavior can be observed upto 1000 Oe applied field. However, from 1000 Oe applied field, FC and ZFC magnetization follows the same trend by reaching a maximum around $T_{\text{max}}$ and it is noteworthy to observe the disappearing of the negative magnetization in ZFC at this point [23,24].

At relatively higher field ($\geq$ 100 Oe), the reason for the difference between the ZFC and FC measurements of the samples is that in the FC the net magnetic moments will preferentially orient in the direction of the applied magnetic field, while in the ZFC the magnetic moment will be magnetically ordered below blocking temperature with their net moments randomly distributed. In a small field applied after the ZFC it will be hard to realign these randomly distributed moments along the field direction as in the FC. However, above a sufficiently high field there will be no difference between the ZFC and the FC (Fig. 5). After 1000 Oe applied field the negative component of the ZFC disappeared and become completely positive by reaching a maximum at $T_{\text{max}}$ and both FC and ZFC follow the same behavior ($\geq$5kOe, Fig. 5).

The bifurcation was observed at 5kOe between the FC and ZFC magnetization at $T_{\text{max}}$. This signifies the onset of spin freezing on the title compound. This is closely related phenomena with the spin glass materials. This bifurcation arises due to quenching the magnetic moment at sufficiently high enough field. In the present study we haven’t studied the field dependent of the freezing temperature. In generally the percentage difference between the FC and ZFC data sets decreases with the applied field. The moving of the transition temperature to lower value with increasing the applied field which is consistent with the notion of a field induced transition or spin flipping due to magnetic frustration. Currently AC susceptibility measurements are underway and that will further prove the identity of the magnetic properties of all these compounds.

**Figs. 5a-c** show the field dependence of magnetization isotherms, obtained at 2, 10, 20 and 30 K, of all the compounds, upto a maximum field of 30 kOe. It can be seen from the figure that none of the studied compounds shows the saturation even at the highest field. However, it may be noticed from these figures that, though all the compounds crystallize in the same structure, the non-saturation tendency is more in the case of $\text{K}_2\text{Fe}_2\text{O}(\text{AsO}_4)_2$. The 2 K magnetization values of the $\text{M}_2\text{Fe}_2\text{O}_5(\text{AsO}_4)_2$ compounds with $M=\text{K}$, $\text{KC}_3$ and Rb, are found to be 0.1683, 0.3039 and 0.2312 $\mu_B/\text{Fe}^{2+}$ respectively in an applied field of 30kOe. However, the $g\mu_B$ value corresponding to $\text{Fe}^{2+}$ is 5 $\mu_B/\text{Fe}^{2+}$.

The large difference between the $g\mu_B$ values and the experimentally observed...
maximum values may be attributed to crystalline electric field effects. It can be seen from Figs. 6 a-c that apart from the non-saturation tendency, another interesting feature is the occurrence of a metamagnetic transition. It may be seen from the figures that the compounds with M= K, KCs and Rb show a metamagnetic transition at critical fields of ~13, 8 and 10 kOe fields, respectively. The single crystals of the title compounds were optically aligned with their chain Fe–O axes and the field dependence of the magnetization was measured on oriented single crystals, applying the field along b axes. On closer examination, of optically aligned single crystals of $\text{M}_2\text{Fe}_2\text{O}(\text{AsO}_4)_2$: along chain axis (b axis) at 2 and 10 K shows steps but at 30 K steps disappears. The metamagnetic transitions seen in these compounds may be attributed to a (1) field induced transition from an antiferromagnetic to a predominantly ferromagnetic state. (2) presence of frustrated triangular in the magnetic lattice, the short Fe–Fe distances within the chains between edge sharing Fe(1)O$_6$ and Fe(2)O$_6$ octahedral or the uniaxial property of the FeO$_6$ chain. It may be mentioned here that such a field induced transition from an antiferromagnetic state to ferromagnetic state has been reported previously [22-24]. It may be recalled here that though the M-T data for KCsFe$_2$O(AsO)$_4$, obtained in a field of 10 kOe, showed the thermomagnetic irreversibility, it was found to be absent in K$_2$Fe$_2$O(AsO)$_4$ and Rb$_2$Fe$_2$O(AsO)$_4$ up to 1kOe. This indicates that the critical field required for a field induced transition from antiferromagnetic state to a predominantly ferromagnetic state is more than 1 kOe in the case of K$_2$Fe$_2$O(AsO)$_4$ and Rb$_2$Fe$_2$O(AsO)$_4$ whereas it is less than 1 kOe in the case of KCsFe$_2$O(AsO)$_4$, which is consistent with the critical field determined from the magnetization isotherms at 2 K.

In order to further understand the nature of the magnetic state of these compounds, heat capacity measurements, under zero-field have been performed. The representative C vs. T plots for all compounds are given in the Fig. 6. The specific heat data shows a $\lambda$-type anomaly with a maximum near 25 K, 21 K and 24 K in K$_2$Fe$_2$O(AsO)$_4$, KCsFe$_2$O(AsO)$_4$ and Rb$_2$Fe$_2$O(AsO)$_4$ respectively. These transition temperatures are exactly matching with magnetization data. This $\lambda$-type anomaly near transition temperature is suggestive of long range magnetic order and nature of zero field heat capacity is very less maintaining the magnetic data. Fig. 6d shows linear change in the C/T vs T$^2$ plots in all the compounds at low temperature due to phonon contributions ($\propto T^2$). Linear contributions ($\propto T$) appear as the extrapolated value for T=0. All the compounds are insulator, and hence a Sommerfeld coefficient $\gamma=0$ is expected. Solid line is extrapolations of the linear part of specific heat at temperature between 7-20 K. The deviation from this linear behavior indicates the presence of a gap in the “quasiparticle” density of in all the compounds. Toward lower temperatures these finite $\gamma$ contributions become suppressed. For K$_2$Fe$_2$O(AsO)$_4$, KCsFe$_2$O(AsO)$_4$ and Rb$_2$Fe$_2$O(AsO)$_4$, this contribution can be estimated to be $\gamma \approx 51, 52.6$ and 55.7 mJ/mol K$^2$ respectively and this value is close to other insulating materials like LaTiO$_3$ [25] and LaMnO$_3$ [26], due to existing orbital order in these two insulator such a contribution is not expected but the experimentally observed $\gamma$ ($\approx$50mJ/mol K$^2$) even larger.

We assume that the opening of gap in a restricted temperature region $T \approx \Delta$ yields $\gamma = \gamma_0 e^{-\Delta/T}$. Plotting the logarithm of $\Delta C_p$ vs. $1/T$ demonstrates that such a type of behavior can indeed be detected, and the representation of fig.6e shows a linear region between 5 to 15K. We are aware that the exponential behavior extends only over a limited temperature range below the gap thus the determined gap value has to be considered as rough estimations only.

![Fig. 6. Specific heat for single crystals of (a) K$_2$Fe$_2$O(AsO)$_4$, (b) CsKFe$_2$O(AsO)$_4$ and (c) Rb$_2$Fe$_2$O(AsO)$_4$. The open circles represent the experimental data and the solid lines are the calculated nonmagnetic contribution. Filled spheres represent the magnetic contribution. (d) specific heat plotted on quadratic temperature scale. The solid line are extrapolated from the linear part $\propto T$ of specific heat at temperatures between 7 to 15 K. (e) $\ln(C/T)$ vs. $1/T$ plot and the solid lines are linear fit assuming $\gamma = \gamma_0 = 50$ mJ/mol K$^2$.

In K$_2$Fe$_2$O (AsO)$_4$, KCsFe$_2$O (AsO)$_4$ and Rb$_2$Fe$_2$O (AsO)$_4$, opening gaps are $\Delta=23.6$ K, 23.9 K and 25 K respectively. In order to analyze the magnetic behavior of these compounds, the magnetic contribution to the heat capacity ($C_{\text{mag}}$) of all these compounds has been determined from the zero-field heat capacity. The $C_{\text{mag}}$ was determined from the zero-field C-T data by subtracting the nonmagnetic contribution from it. The $C_{\text{lattice}}$ and $C_{\text{elec}}$ contributions to the heat capacity were determined using equation 1. $M_2$Fe$_2$O (AsO)$_4$ compounds have orthorhombic structure and hence a simple Debye model is not a good approximation for calculating the lattice contribution to the heat capacity. Therefore, the modified expression taking into account the Debye and the Einstein models, as represented by the second and third terms of eqn. 1 was used to analyze the C-T data [27-31].
where, $\theta_E$’s and $\theta_D$ are the Einstein and Debye temperatures, respectively. In the equation 1 that the first term corresponds to the electronic contribution to the heat capacity whereas the second and third terms are due to the phonon contribution corresponding to the Einstein and Debye models, respectively. The coefficients $\alpha_i$’s have been put to take care of the anharmonicity effects [32, 33].

It may further be noticed from equation 1 that in the second term corresponding to the Einstein model, the summation extends from $i=1$ to 42, which is due to the 42 different optic branches expected in the $M_2FeO(AsO_3)_2$ compounds. However, in the calculation of the $C_{lattice}$ three different $\theta_E$’s, two corresponding to a group of 12 optic branches and third one corresponding to 18 Optical branches, are taken into consideration. Fig. 8a, b & c show the temperature variation of the total heat capacity, the nonmagnetic contribution and the magnetic contribution of the $M_2FeO(AsO_3)_2$ compounds with $M=K$, KCs and Rb respectively. The parameters used for calculating the nonmagnetic contribution to the heat capacity are given in Table 2.

![Table 2. Values of coefficient of electronic specific heat (γ), Debye temperature (θD), Einstein temperatures (θE), gap (Δ) and the anharmonicity coefficient (α) of the $M_2FeO(AsO_3)_2$ compounds.](image)

It can be seen from Fig. 6a, b & c that the $C_mag$ starts increasing at temperatures well above $T_{ord}$ and shows a hump. The occurrence of the hump in $C_{mag}$-T plot of these compounds may be attributed to Schotky anomaly arising due to the crystalline electric field levels. It may be mentioned here that the $C_{mag}$ at low temperatures shows $T^3$ dependence (shown in fig 6f, similar behavior observed in other two compounds also) and therefore indicates that the low temperature magnetic state in these compounds are antiferromagnetic [35].

### Conclusion

In summary $M_2FeO(AsO_3)_2$ is one of the few magnetic insulators that show stepped magnetization and complex FC an ZFC behavior. The key component in such a complex magnetic system may arise due to the diversity of the bond angles and bond distances in FeO$_6$ wires in $M_2FeO(AsO_3)_2$. The first crystallographically distinct Fe sites, Fe(1) and Fe(2) may have a magnetic moment that points directly along the b axis, while both sites or one site may share a magnetic component significantly in another direction by giving a canted magnetic moment along the chain direction.

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### Author’s contributions

All authors have equal contributions. Authors have no competing financial interests.

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