The $M_3Fe4V_6O_{24}$ (M = Cu, Zn, Mg, and Mn) Studied at High Temperatures using EPR_2

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ABSTRACT

In the high temperature range (293 K to 493 K), electron paramagnetic resonance (EPR) spectra of $M_3Fe_4V_6O_{24}$ (M = Cu, Zn, Mg, and Mn) compounds were examined. The role of magnetic (Cu, Mn) and non-magnetic (Zn, Mg) ions in the production of magnetic resonance spectra in the $M_3Fe_4V_6O_{24}$ structure was investigated. The effect of temperature on EPR parameters such as resonance field, line width, and integrated intensity was investigated. In terms of distinct relaxation mechanisms and magnetic interactions in spin systems, similarities and variations in the temperature behaviour of these parameters have been studied. Additional magnetic ions (M = Mn or Cu) play a key role in the $M_3Fe_4V_6O_{24}$ structure, and the consequences have been studied.

Keywords-- Epr, High Temperatures, Compounds, Properties

I. INTRODUCTION

The $M_3Fe_4V_6O_{24}$ (M = Cu, Zn, Mg, Mn, and Co) compounds have been studied for a long time because of their intriguing physical features and potential applications. Some of these are members of the howardevansite mineral group, and two new minerals of this sort were recently found in volcanic ash from Kamchatka's most recent eruptions. The crystal structures of $M_3Fe_4V_6O_{24}$ powders (M = Cu, Zn, Mg, and Mn) were determined using XRD and neutron diffraction methods. Three sub lattices are related to metal ions in the structure, two of which are associated with iron ions. In the M ion site, magnetic or diamagnetic ions can occupy the M ion site, resulting in a more complicated magnetic system in the former scenario. At high temperatures, the Curie-Weiss behavior, = C/(T−), dominates with a negative Curie-Weiss temperature (the maximum value for the compound M = Mn and the least for M = Cu).It's worth noting that adding a strong magnetic ion to the M site raises the value, whilst adding a weak magnetic ion, like copper, lowers it. At low temperatures, magnetic fracturing mechanisms have been seen.

A symmetrical, strong, and broad line characterizes the principal electron paramagnetic resonance (EPR) spectrum in all examined substances. The compounds with M = Mn and Cu also show lines produced from manganese and copper ions with varying spin-lattice relaxations. The compound M = Mn has the maximum EPR amplitude at room temperature, although the line width of this resonance line is the smallest. The resonance line parameters for the compounds M = Zn and Mg are identical, and the M = Cu compound behaves similarly to the M = Mn sample. As a result, it is clear that the presence of magnetic ions (M = Cu and Mn) has a major impact on the relaxation processes and that the larger the magnetic moment, the more dramatic the change in the EPR parameters of that compound. Despite the fact that their crystalline structures are well understood, determining the magnetic centers responsible for the creation of the observed EPR spectra is one of the major challenges. The presence of magnetic clusters in these compounds is seen to have a high likelihood, according to The occurrence of ferromagnetic resonance (FMR) lines in EPR spectra is not ruled out in this scenario. Many disparities between DC magnetic susceptibility and magnetic resonance data could be satisfactorily explained under this premise. Furthermore, magnetic competition effects due to the presence of various magnetic sub lattices were found in the investigated compounds at a temperature of around 200 K.

The purpose of this study is to examine the EPR spectra of four $M_3Fe_4V_6O_{24}$ (M = Cu, Zn, Mg, and Mn) samples recorded at temperatures ranging from 293 K to 493 K. Each sample contains magnetic Fe ions as well as a second magnetic ion in two of them (Cu or Mn). Comparison of the acquired results and discussion of the observed differences in terms of the presence of an additional magnetic ion in the crystal structure would be enlightening. This research could assist in understanding which magnetic centres are involved in the formation of EPR spectra and the nature of magnetic interactions between them.

II EXPERIMENTAL

Previous papers described the process of preparation and chemical characterization of the powder samples under investigation. In addition, previous articles have included thorough structural analyses. On a Ra-

diopan SE/X 2544-M spectrometer fitted with a handmade high-temperature unit, EPR measurements in the region of 293 K to 493 K were performed.

III. DISCUSSION

The EPR spectra of four investigated $M_3Fe_4V_6O_{24}$ (M = Cu, Zn, Mg, and Mn) samples recorded at various temperatures in the high-temperature range are shown in Figure 1. For all four examined substances, a symmetric and powerful resonance line was found across the whole temperature range studied. The Lorentzian line shape function was $(g_{eff} = \frac{h\#}{B B_r}$, while the integrated inten- successfully fitted to the observed spectra, just as it had been done earlier at lower temperatures. The temperature dependency of the predicted EPR spectra parameters: effective g-factor (geff), peak-to-peak line width (DBpp), and integrated intensity (Iint), as well as the inverse of integrated intensity (1/Iint), can be seen in Figs. 2–4. From the resonance field Br at the resonance condition, the effective g-factor was calculated.

This was supposed to be the case when Iint = A DB2pp, where A is the amplitude of the EPR signal in the first derivative mode. The g-factor reduces marginally when the resonance field increases with increasing temperature when the samples are heated over 340 K. A reverse process is visible for compounds having magnetic ions at the M (II) site at temperatures of about 450 K. In the temperature range of 340 K to 450 K, the shift of the resonance field Br (defined as Br = Br(T) – Br(T + DT)) exhibits a roughly linear temporal dependence (Fig. 2).The Br/DT temperature gradients of the resonance field shift were estimated as follows: Br/DT=7 x 10^3 mT/K for $Cu_3fe_4V_6O_{24}$,Br/DT= 6 x 10^3 for $Zn^3Fe_4V_6O_{24}$,Br/DT = 6 x 10^3 mT/K for $Mg_3 Fe_4V_6O_{24}$ and Br/DT = 9 x 10^3 mT/K for $Mn_3Fe_4V_6O_{24}$ The presence of additional metallic ions (Cu and Mn) in the crystal structure raises the temperature gradient's value.

The DBpp line width is shown in Fig. 3 as a function of temperature. The line width reduces monotonically with rising temperature for the two compounds with magnetic ions in the M ion site, whereas at around 400 K, the line width of $Zn^3Fe_4V_6O_{24}$ and $Mg_3Fe_4V_6O_{24}$ increases with increasing temperature. A closer look at Fig. 3 reveals that three questions should be addressed consistently: (a) why does the line width decrease with increasing temperature for all investigated samples below 400 K; (b) why is the line width smaller for compounds with additional magnetic ions (M = Cu and Mn); and (c) why does the line width increase above 400 K only for M = Zn and Mg compounds. A well-known consequence is the narrowing of line width as the temperature rises. It has been found in a variety of compounds, and the temperature-dependent exchange narrowed spin-spin interaction is frequently invoked to explain it. The role of the exchange narrowing mechanism will be discussed in greater depth later.
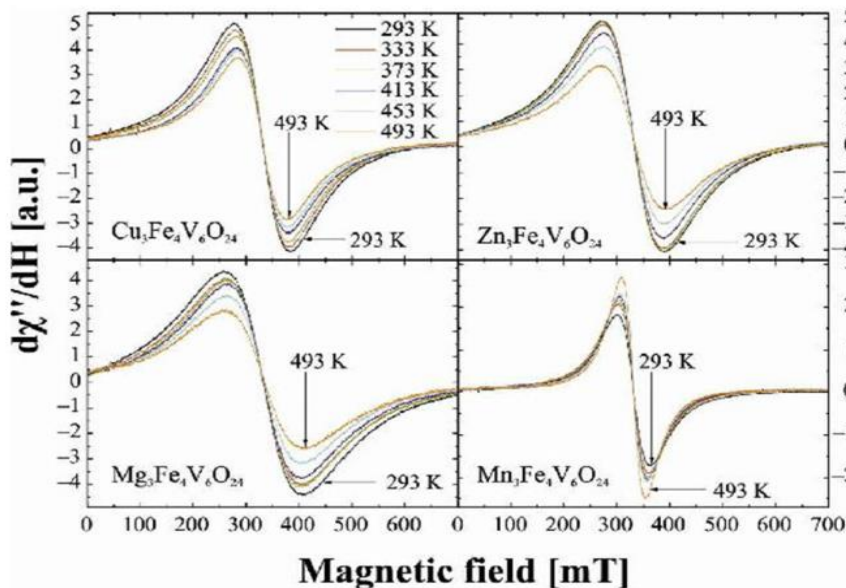

Figure 1: shows the EPR spectra of the examined $M_3Fe_4V_6O_{24}$compounds at various temperatures

The temperature dependency of the EPR integrated intensity (Iint) and its reciprocal (1/Iint) are shown in Figure 4. At microwave frequencies, the EPR integrated intensity is proportional to the magnetic

susceptibility of the spin system under investigation. In the temperature range of 333 K to 433 K, the EPR integrated intensity follows the Curie-Weiss law, Iint = C/(T) where the constant C is related to an effective magnetic moment and the Curie-Weiss temperature is positive for ferromagnetic interaction and negative for antiferromagnetic interaction between the involved spins. The following values were estimated for Cu, 48 (4) K for Zn, 17 (11) K for Mg, and −170 (30) K for Mn compounds: 56 (15) K for Cu, 48 (4) K for Zn, 17 (11) K for Mg, and −170 (30) K for Mn compounds. $Cu_3Fe_4V_6O_{24}$ and $Mn_3Fe_4V_6O_{24}$ are the most likely to interact.
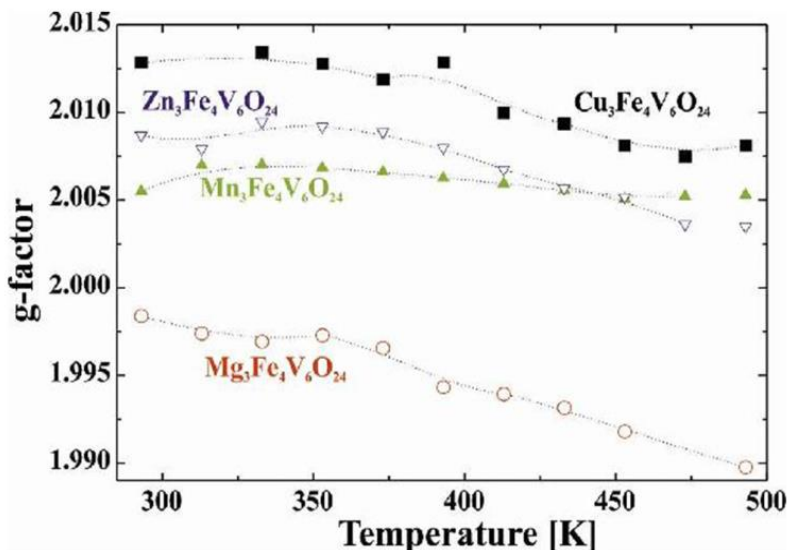

Figure 2: The Geff-factor in $M_3Fe_4V_6O_{24}$ compounds is temperature dependent. The size of the points is smaller than the standard uncertainty in geff-factor values. Dotted lines serve only as eye cues
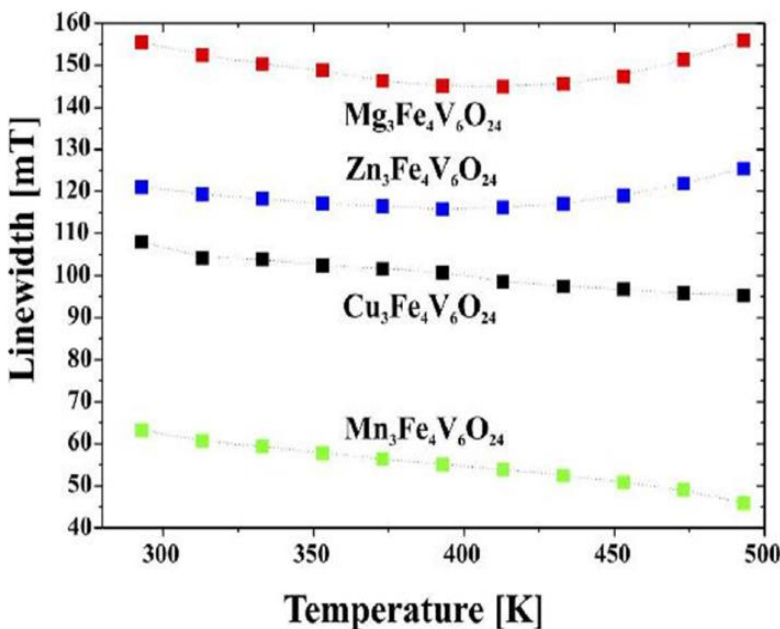

Figure 3: The line width DBpp in $M_3Fe_4V_6O_{24}$ compounds is temperature dependent. The diameters of the points are smaller than the standard uncertainties in DBpp values. Dotted lines are simply eye cues

Two separate magnetic ions are present in the crystal structure of compounds containing two different magnetic ions. It's worth noting that the sign of may change as the temperature rises from low (below RT) to high (above RT). Because the Curie-Weiss temperature is a measure of effective interaction strength and type, a shift

in its sign can be interpreted as a shift in the leading interaction type (ferromagnetic $ antiferromagnetic). The crystal structures of $M_3Fe_4V_6O_{24}$ compounds if they contain a number of different magnetic sub lattices with different sorts.
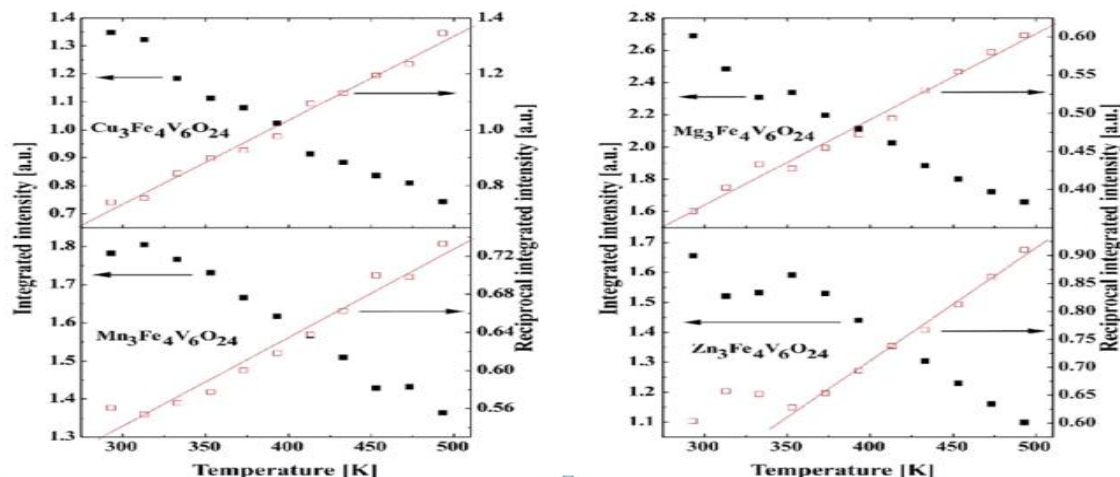

Figure 4: The integrated intensity Iint (left axis) and reciprocal integrated intensity (right axis) of $M_3Fe_4V_6O_{24}$ compounds are temperature dependent

Integer values have standard uncertainties that are smaller than point sizes. Less-squares fitting to the experimental points are shown as solid lines.
The magnetic interactions, and if their strength varies with temperature, the observed phenomenon of sign change near to RT could be the result.
As shown in Fig. The relationship between the Curie-Weiss constant C and the Curie-Weiss temperature is seen in Figure 5. The $Cu_3Fe_4V_6O_{24}$ and $Mn_3Fe_4V_6O_{24}$ compounds have a smaller effective magnetic moment than $Zn_3Fe_4V_6O_{24}$ and $Mg_3Fe_4V_6O_{24}$, indicating the presence of an antiferromagnetic interaction between Fe and Cu/Mn ions. This interaction must be particularly

strong in $Mn_3Fe_4V_6O_{24}$ as it overcomes the weaker ferromagnetic interaction in Fe sub lattice, resulting in an anti-ferromagnetic total effective interaction, as demonstrated by the negative sign of the Curie-Weiss temperature. Magnetic frustration due to clustering of magnetic ions at low temperatures is not ruled out in the case of $Cu_3Fe_4V_6O_{24}$ and $Mn_3Fe_4V_6O_{24}$ compounds.
The Lorentzian shape is widely recognized when the shortening of the resonance line is caused by temperature-dependent exchange interaction. All of our EPR spectra are the same. Because the exchange-narrowing spin-spin.
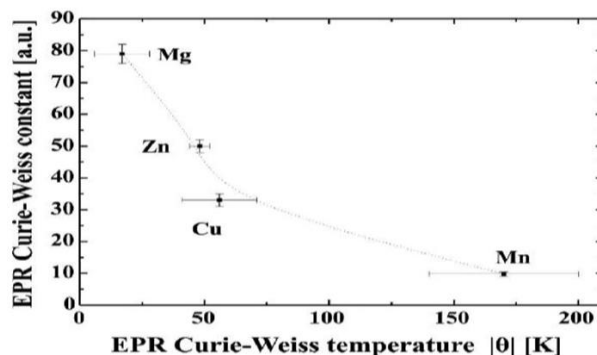
Figure 5 shows the relationship between the Curie constant C and the Curie-Weiss temperature for all samples studied. The dotted line is merely a visual aid

Interaction between Fe ions is active in all four investigated compounds, the line narrowing observed below 400 K is explained. In most cases, the exchanged-narrow line width is computed using the equation DB = DB2dip/Bex, where DBdip is the dipolar line width determined by the dipol-dipol interaction experienced by each spin from all of its adjacent spins, and Bex is the temperature-dependent exchange field. Given that Bex is proportional to the Curie-Weiss temperature, then Bex, the exchange constricted line width, will be inversely proportional to This explains why the line widths of our four samples at temperatures below 400 K are ordered in that way: samples with two distinct magnetic ions have stronger magnetic interactions and consequently narrower EPR lines than compounds with one Fe magnetic ion.

Another dynamic relaxation process takes place above 400 K in $Zn_3Fe_4V_6O_{24}$ and $Mg_3Fe_4V_6O_{24}$, compounds (Figure. 3). As a result, as the temperature rises, the line width in both samples begins to widen. In general, a direct spin-phonon process (modulation of the crystalline electric field by lattice vibration involving one phonon in the relaxation process), modulation of the static Dzyaloshinsky-Moriya interaction between a pair of magnetic ions by a single phonon, and the bottleneck scenario involving relaxation of localized magnetic moments to the lattice via the highly molecular Moriya interaction all. The first process appears to operate in our two Zn and Mg compounds, whereas the second mechanism is normally achieved in spin system S = 1/2, and the third mechanism does not require a considerable change in the g-factor, contrary to what we detect in our samples (Fig. 2). The inclusion of additional magnetic ions magnifies the exchange narrowing processes by increasing and frustrating exchange interactions between magnetic ions in $Mn_3Fe_4V_6O_{24}$ and $Cu_3Fe_4V_6O_{24}$ compounds, which either suppresses or moves this spin-lattice mechanism to much higher temperatures.

IV. CONCLUSION

In the high temperature range, the EPR spectra of four compounds $M_3Fe_4V_6O_{24}$ (M = Cu, Zn, Mg, and Mn) were examined. The temperature dependence of the resonance field, as well as the line width and integrated intensities of the observed single and intense Lorentz an line, has all been determined. The observed line is narrowed in all examined compounds at T 400 K, and the effect is significantly stronger in $Mn_3Fe_4V_6O_{24}$ and $Cu_3Fe_4V_6O_{24}$ compounds with an extra magnetic ion at the M site. Dependence of the resonance field and integrated intensity may also be used to infer the presence of two different magnetic ions in the $M_3Fe_4V_6O_{24}$ structure. As a result, the more intricate magnetic structures of $Mn_3Fe_4V_6O_{24}$ and $Cu_3Fe_4V_6O_{24}$ compared to $Mg_3Fe_4V_6O_{24}$, and $Zn_3Fe_4V_6O_{24}$ compounds cause ferromagnetic and antiferromagnetic interactions to compete, resulting in the formation of magnetic frustration effects.

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