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ARTICLE

Magnetic Properties of Co^{II}, Co^{III} and Co^{II-III} Coordinated to a Carbosilazane-Based Polymer

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Abstract: Magnetization measurements have been performed on Co^{II}, Co^{III} and Co^{II-III} incorporated into carbosilazane-based polymeric matrix (PEDCSZ, $-[(CH_3)_2SiNHCH_2CH_2NH]_n$--). The local field effect has been evaluated using simple approach similar to the Weiss molecular field model in the paramagnetic state. In this approach, the exchange interaction is represented by the average molecular field constant γ. The calculated γ values are 327, 100 and 223 Oe-g/emu and the corresponding average molecular fields are: 2.7, 0.70 and 2.0 kOe for Co^{II}, Co^{III} and Co^{II-III}, respectively. The corresponding molecular field values are about four orders of magnitude lower than that in elemental Co metal. The magnetic measurements support the notion that coordination of this polycarbosilazane matrix with different valences of Co ions has pronounced effects on the exchange interaction and on the general magnetic properties of the system. The results also indicate that the strongest exchange effects are in the Co^{II} case, and that the magnetic properties in the mixed valance Co^{II-III} case do not follow the simple "Additive Rule".

Keywords: Magnetization; Polycarbosilazane; Molecular Field; Paramagnetism; Antiferimagnetism; Exchange Interaction; Coordination and Magnetic Moments.

Introduction

The magnetic behavior of molecular, macromolecular, polymeric and extended lattice systems containing unique magnetic centers attracts the interest of researchers working in a wide variety of disciplines including biomedical diagnosis and treatment, biotechnology, catalysis, magnetic recording, microwave antennas among others [1-5]. Recent advances in plastic antennas rely on using common transition metals such as cobalt, nickel and iron as alternatives to rare-earth based magnetic materials [5]. On the other hand, the presence of isotropic and anisotropic interactions leading to different levels of magnetic coupling or magnetic ordering is of prime importance in magnetic clusters, low-dimensional, 3-dimensional and core-shell molecular magnetic systems [6-8]. Unlike physical dispersion of nano-scale magnetic particles in a polymeric matrix, chemical coordination of magnetic ions to polymer backbone results in a regular

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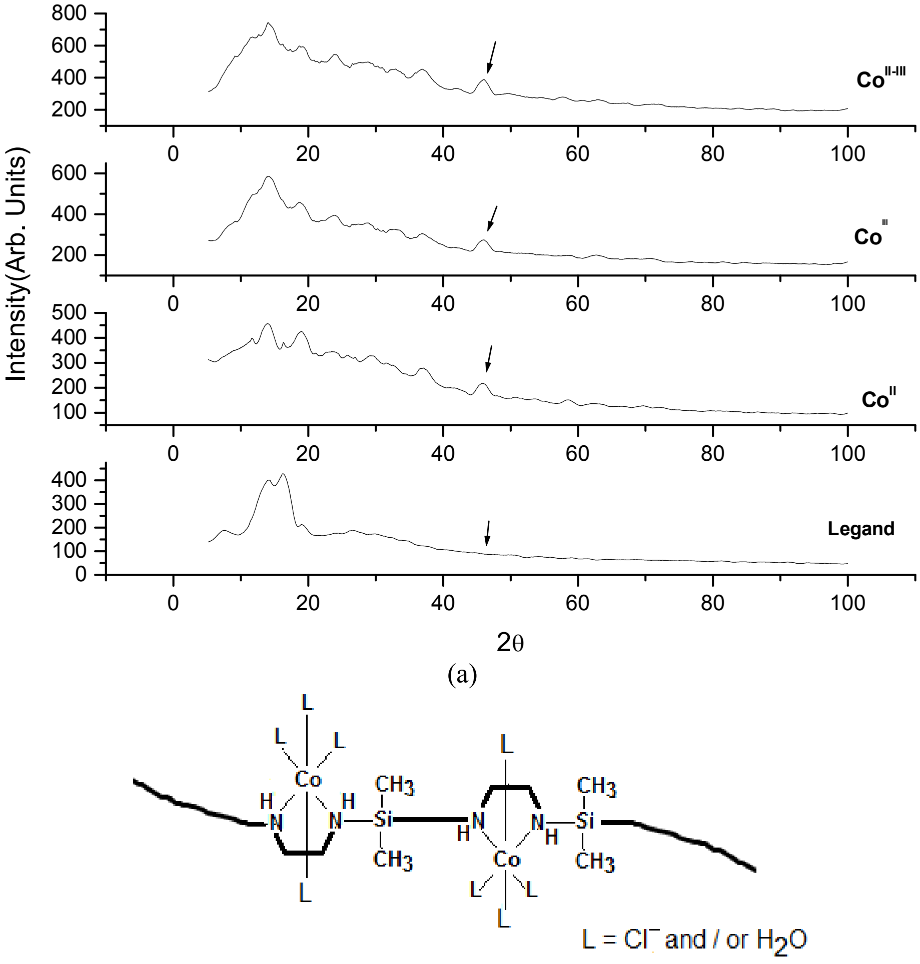
distribution of magnetic sites at the molecular levels. In such a case, the presence of isolated magnetic spin sites allows one to examine in details spin-spin interaction, spin delocalization, spin-crossover, spintronics and spin-frustrated assemblies. Such interaction is critical in evaluating the performance of soft-hard magnetic materials. Furthermore, combination of magnetic and optical properties to generate switchable photo-magnetic materials is finding increasing interest in spintronics applications. The fundamental magnetic properties of elemental Co^{0}, Co^{II} and Co^{III} and their magnetic interactions in molecular magnets, magnetic polymers and alloys have been extensively studied in recent years [6-8]. Generally, cobalt is added to Fe to increase the saturation magnetism in antennas-based cobalt ferrites [8].

This article is part of our continuing interest in low-dimensional magnetic arrays, where the magnetic sites are attached at regular intervals in fixed position [9-10]. In a previous publication, we examined the dielectric behavior of the divalent (d^{7}) Co^{II}, trivalent (d^{6}) Co^{III} and mixed-valence (d^{7}-d^{6}) Co^{II-III} containing polycarbosilazane polymer (PEDCSZ, –[(CH$_3$)$_2$SiNHCH$_2$CH$_2$NH]$_n$--), Fig. 1, and found out that the divalent Co^{II} system exhibited the higher bulk resistance compared to the trivalent Co^{III} and mixed-valent Co^{II-III} analogs [11], reflecting high localization of electrons. In this work, we extend our interest to examine the spin delocalization / spin interaction of this system. In particular, we present results which support the notion that coordination of these cobalt ions with PEDCSZ greatly affect the spin-spin exchange interaction and therefore their magnetic characteristics. In this respect, we found that the strongest exchange effect occurs in the Co^{II} system, and that the magnetic properties in the mixed-valance Co^{II-III} system do not follow the simple "Additive Rule".



(a)

(b)

FIG. 1(a). XRD pattern for PEDCSZ legand and Cobalt ions-coordinated polymers. (b) Schematic representation of Co^{II}, Co^{III} and Co^{II-III} chloride salts incorporated into the PEDCSZ matrix.

Experimental Section

The detailed procedure for the synthesis and sample preparations of the examined Co^{II}, Co^{III} and Co^{II-III} containing PEDCSZ has been published earlier [11]. For the magnetic measurements, several milligrams of the powdered materials were encapsulated in small non-magnetic plastic vile. The magnetic moment of the empty vile falls within the noise signal (10^{-5} emu) of the VSM used to monitor the magnetic moment. The magnetization measurements (*M vs. H* and *M vs. T)* were recorded using PAR-4500/150A 9-tesla vibrating sample magnetometer (VSM) in the temperature range 2 to 300 K. A calibrated carbon glass resistor located near the specimen was used to monitor the temperature. A pure Ni-standard was used to calibrate the magnetometer. The overall accuracy in the temperature measurements is better than 0.1K.

Results and Discussions

(a) XRD Results

Fig. 1(a) shows the XRD patterns for the PEDCSZ along with the Co^{II}, Co^{III} and Co^{II-III} coordinated polymers. The patterns were recorded at room temperature using Cu K_α radiation (λ=1.5418 Å), in the 2θ range 5° to 100° with a step size of 0.03° operating at 30 kV and 30 mA. The XRD pattern of PEDCSZ displays two diffuse broad diffraction peaks centered in the 10°-20° and 20°-40° regions, suggesting that PEDCSZ is amorphous in nature. However, the XRD patterns for the cobalt-containing PEDCSZ under investigation show that the degree of crystallinity of the samples increased with the insertion of Co^{II} and Co^{III} ions in the system. Moreover, the diffused peak of the PEDCSZ become more broadened due to the incorporation of Co ions in the polymer backbone. The crystallite size of these samples was estimated using Scherer's Equation ($D_m = K\lambda/[\beta \cos\theta]$, where K is a constant, λ is the wavelength of X-rays, β is the full width at half maximum and θ is the diffraction angle) [12-13]. Based on the widening of the peaks centered at $2\theta = 46^o$, the crystallite size for Co^{II}, Co^{III} and Co^{II-III} containing PEDCSZ is found to be comparable (D ≈10 nm) showing fine particle magnetic systems. Furthermore, the peak at $2\theta = 14.8^o$ is used to estimate the chain separation of the PEDCSZ which gives a d-spacing of 6.00Å (Braggs′ Law, $n\lambda = 2\, d \sin\theta$). The attachment of Co^{II}, Co^{III} and Co^{II-III} increased the chain separation of the PEDCSZ from d = 6.00 Å in metal free matrix to d = 6.32, 6.26 and 6.30 Å, respectively. This slight increase in d-spacing clearly suggests that the cobalt ions are entrapped between the PEDCSZ chains, Fig. 1(b) [9]. The comparable separation distances show that magnetic differences cannot be attributed to spin-spin distance.

(b) Magnetic Results

Fig. 2 shows the variation of magnetization *M* with temperature *T* at a constant applied magnetic field $H=10^4$ Oe for the three samples Co^{II}, Co^{III} and Co^{II-III} containing PEDCSZ, respectively. *M* exhibits a sharp drop with increasing temperature at low values of $T<20$K then decreasing very slowly with *T,* suggesting that the three systems undergo a transition from an ordered phase to disordered (paramagnetic) phase. The phase transition occurs at T~17K, as can be clearly shown in the inset of Fig. 2.

The sample doped with Co^{II} reveals the sharpest minimum, which reflects a sharper transition to the paramagnetic state, while the Co^{III} sample showed wider minimum and broader transition to the paramagnetic state. The sample with mixed-valance states Co^{II-III} occurs in between. This would suggest that the sample with Co^{II} ions exhibits a relatively larger magnetic exchange interaction.

Fig. 3 shows the selected isothermal curves of the magnetization, *M*, (in emu/g) *versus* the applied magnetic field, *H*, (in Oe) in the temperature range 4.2K–60K for the three samples of Co^{II}, Co^{III} and Co^{II-III} coordinated PEDCSZ. The curves show no hysteresis or remanence. As it is clear from Fig. 3, the magnetization increases rapidly with *H* at temperatures ($T<15$ K) and fields ($H<10^4$ Oe). This is similar to a ferromagnetic behavior that is commonly seen at very low magnetic fields. At higher fields, the magnetization increases linearly indicating the approach to saturation after subtraction of the linear high field susceptibility. At temperatures $T\geq20$K, the magnetization increases linearly with the applied magnetic field, suggesting paramagnetic behavior. The ferromagnetic ordering was tested using the Arrott plots[14], where M^2 *versus* H/M curves are drawn for the three samples and are shown in Fig. 4. These curves, at low values of

H/M, pass through the *H/M* axis as seen in Fig. 4. The nonexistence of intercept with the M^2 axis at small values of *H/M* does not mean that there is no spontaneous magnetization. This is clear from the curvature of the Arrott plots curves at low temperatures. The rapid increase in the magnetization at low temperatures and low fields can be attributed to the formation of fine, as mentioned in the XRD results, superparamagnetic clusters of Co-complexes. This is further supported by the enhanced values of the average molecular field constant γ (the exchange interaction).

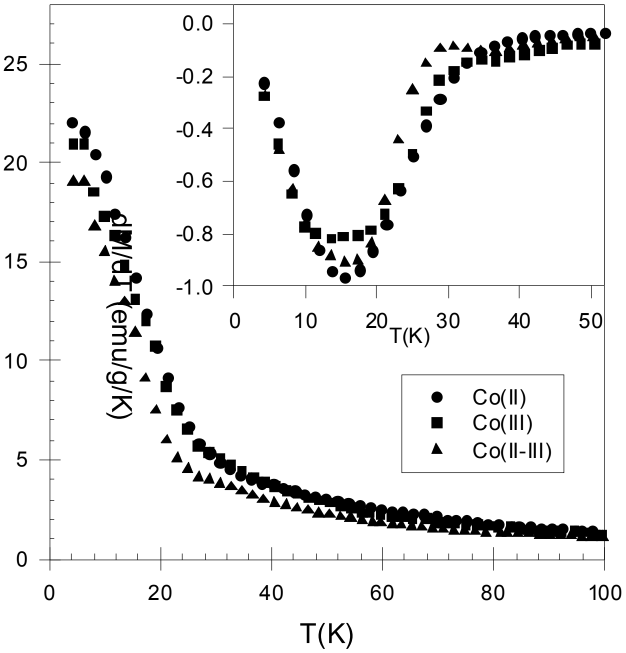
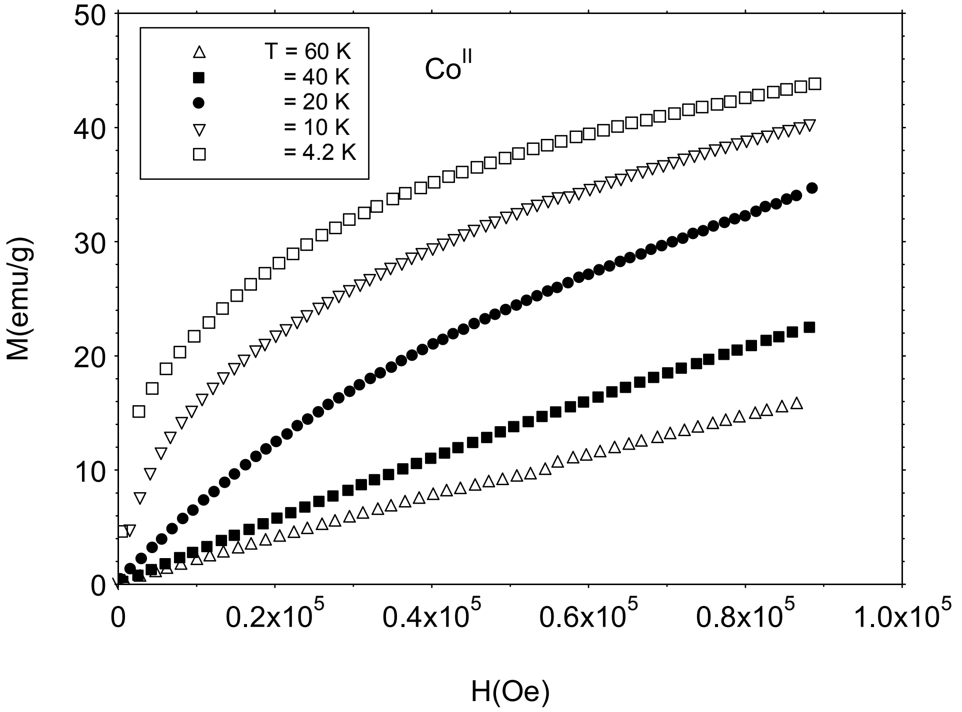


FIG. 2. Variations of the magnetization with temperature. The inset is the derivative of the magnetization with respect to temperature.



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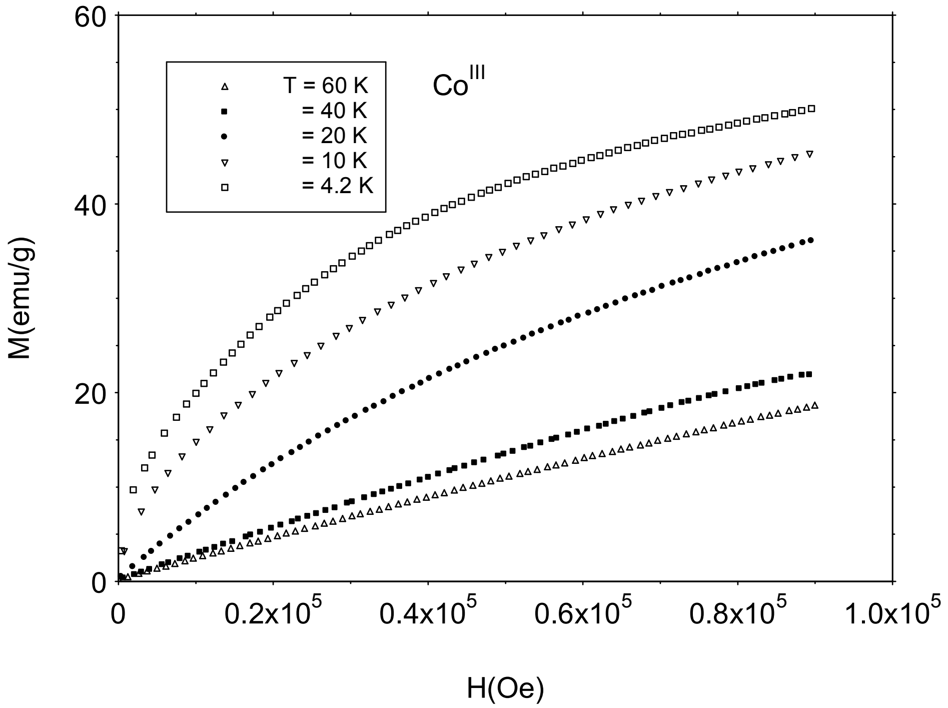

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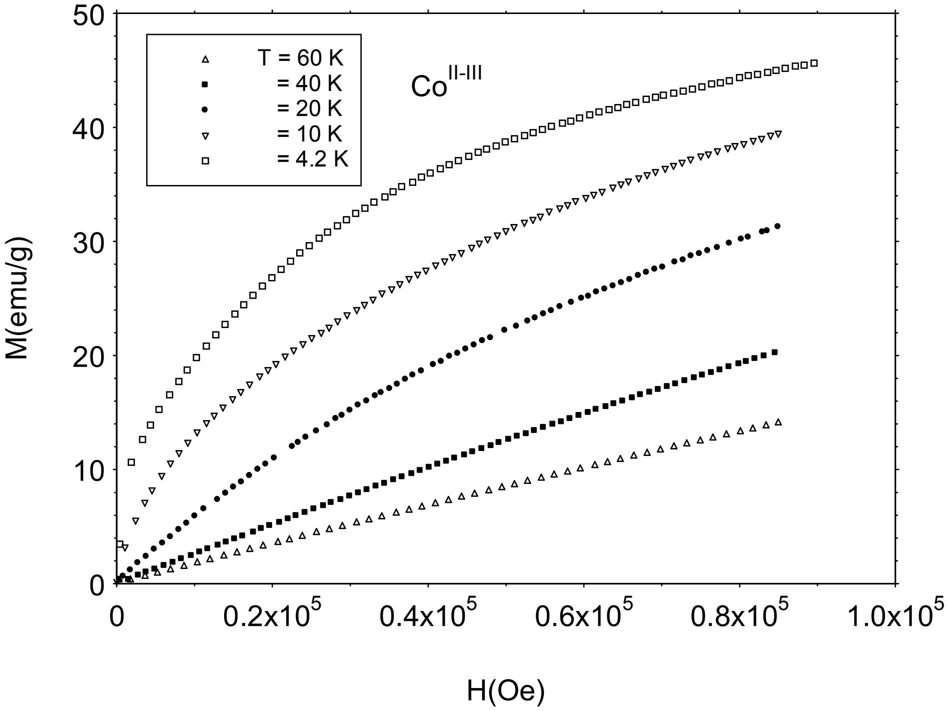
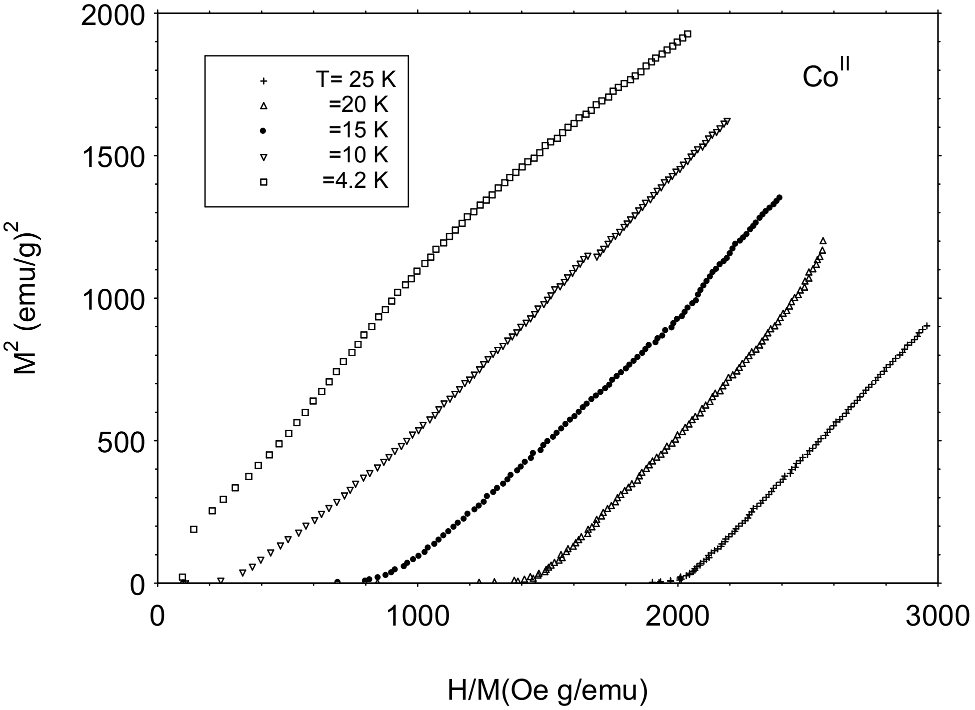
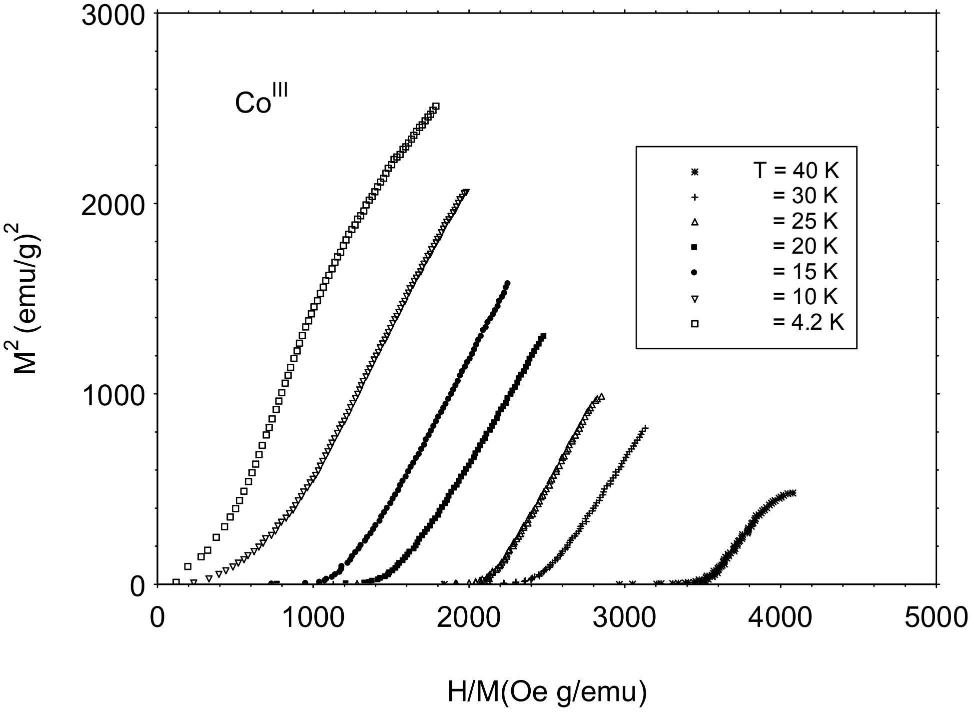


(c)

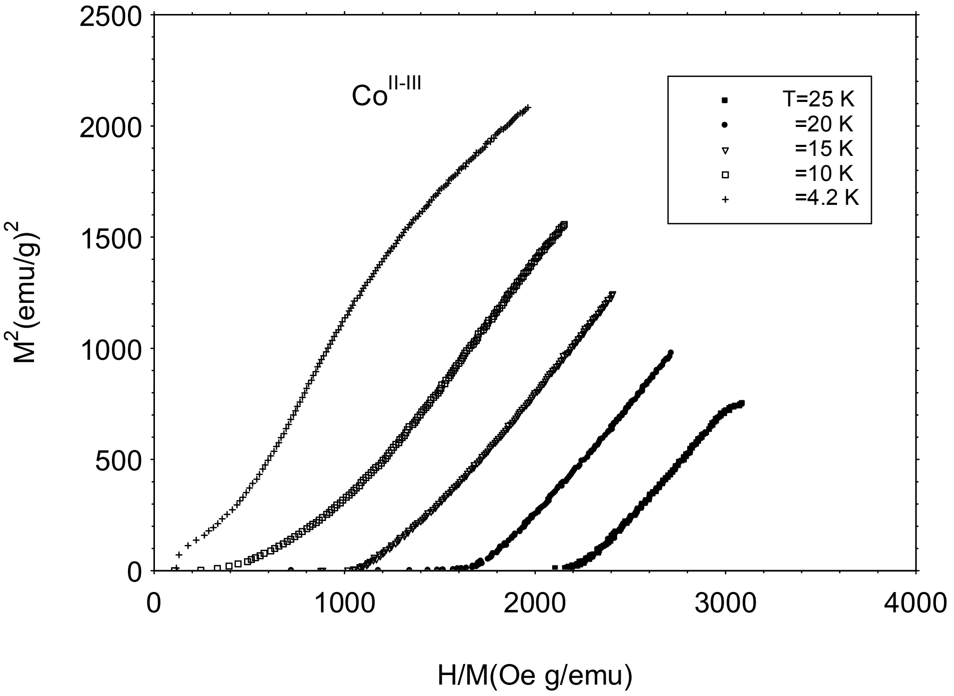
FIG. 3. Selected isothermal curves of the Co - ions coordinated polymers (a) Co^{II}, (b) Co^{III} and (c) Co^{II-III}.


Co^{II}
T= 25 K
=20 K
=15 K
=10 K
=4.2 K
M^2 (emu/g)^2
H/M(Oe g/emu)
0
500
1000
1500
2000
0
1000
2000
3000

(a)


Co^{III}
T = 40 K
= 30 K
= 25 K
= 20 K
= 15 K
= 10 K
= 4.2 K
M^2 (emu/g)^2
H/M(Oe g/emu)
0
1000
2000
3000
0
1000
2000
3000
4000
5000

(b)



(c)

FIG. 4. Arrott plots of the three Co-ions coordinated polymers (a) Co^{II}, (b) Co^{III} and (c) Co^{II-III}.

The existence of two magnetic phases, superparamagnetic and paramagnetic, can be explained by expressing the total magnetization as [15]:

$$M(T) = M_s(T)L(a) + \chi_h(T)H$$

$$M(T) - \chi_h(T)H = M_s(T)L(a) \qquad (1)$$

where $M_s(T)$ is the saturation magnetization at temperature T, $L(a)$ is the Langevin function given as $L(a)=coth(a)-1/a$, $a=\frac{\mu H}{k_B T}$, μ is the magnetic moment, k_B is the Boltzmann constant and $\chi_h(T)$ is the high field induced susceptibility. $\chi_h(T)$ was calculated using the high field data of the isothermal curves and is presented in Fig. 5 as χ_h *versus T*. Initially, χ_h increases with increasing temperature; reaching maximum near 20K then gradually decreases. The high field induced susceptibility maximum may indicate break-down of the superparamgnetic cluster to a paramagnetic behavior above 20K.

The magnetization curve (Fig. 3; T= 4.2K) for Co^{II} starts with a slope higher than that of Co^{III} and Co^{II-III} coordinated polycarbosilazane. This supports the conclusion that Co^{II} has a higher exchange interaction. The three samples show a Curie-Wiese paramagnetic behavior. The magnetic properties in the mixed valance coordinated polymer Co^{II-III} do not follow the simple “Additive Rule”.

The magnetization curves approach saturation with finite slope at high fields (up to 9 Tesla). Moreover, the Co^{II} magnetization nearly saturates at slightly lower magnetization than that for the other two samples Co^{II-III} and Co^{III}, respectively. In the paramagnetic region, the magnetization curves for all samples increase linearly with the applied field.

Molecular Field

The Weiss molecular field model can be easily applied to paramagnetic materials, where the magnetic spins behave almost independently from each other. The interaction between the spins will affect the local spin environment, giving rise to non-vanishing molecular field (H_m). Isothermal curves fitted to equation 1 do not give satisfactory fit to the experimental data. In order to achieve a reasonable fit, the molecular field effect has to be accounted for in any M *versus* H_{ef}/T representation; where $H_{ef} = H+H_m$, $H_m = \gamma M$ and γ is the exchange interaction constant[16]. In this representation, the applied field, H, is replaced by an effective field, H_{ef}.

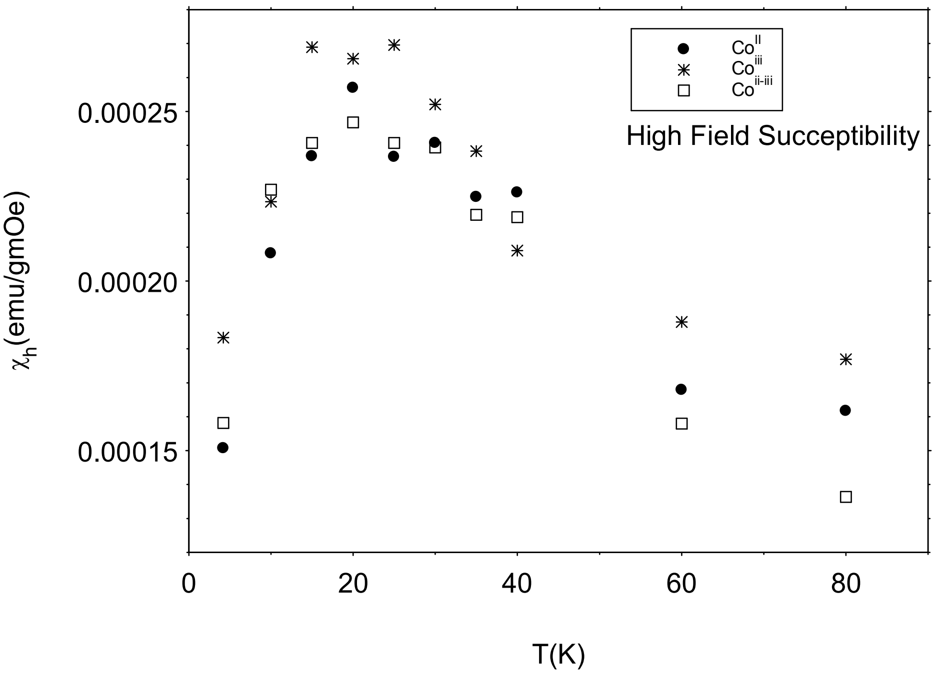


FIG. 5. Variations of the high field susceptibility with temperature.

A simple approach is used to determine γ, and this is explained below. According to the classical theory of paramagnetism, the magnetization, M, can be expressed as a function of H_{ef}/T.

$$M = f\left(\frac{H + \gamma M}{T}\right) \qquad (2)$$

where:

$$\frac{H}{T} + \frac{\gamma M}{T} = f^{-1}(M) \qquad (3)$$

Equation (3) is used to determine different values of γ at constant values of magnetization as shown in Fig. 6. Although the values of γ depend on the temperature as found in other systems [17-18], a constant average value of γ for each sample was used. This can be justified, since the behavior of all samples for T>20K is paramagnetic. The estimated values of γ are 327, 100 and 223 (Oe-g/emu) and the corresponding molecular fields are 2.7, 0.70 and 2.0 kOe for Co^{II}, Co^{III} and Co^{II-III} samples respectively.

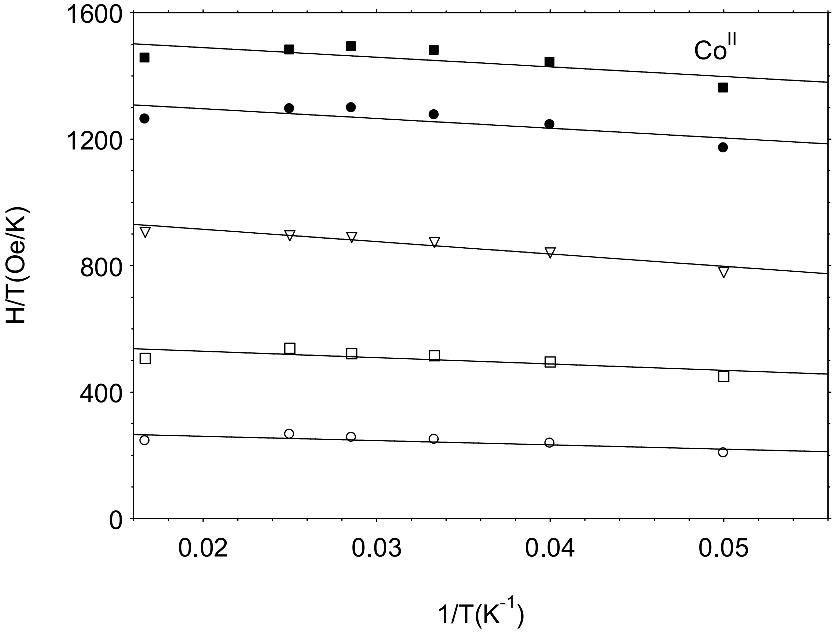
It is worth mentioning that the value of γ for Co^{II-III} sample is different from the γ values for the other two samples. Incidentally, it equals the difference between the values for the other two samples Co^{II} and Co^{III}. Similarly, the calculated molecular field for Co^{II-III} is different from the corresponding values for the other two samples; however it equals the difference between the values for the other two samples Co^{II} and Co^{III}. This may reflect an antiferrimagnetic coupling between Co^{II} and Co^{III} atoms in Co^{II-III} sample. This antiferrimagnetic coupling behavior is due to the coordination of Co^{II} and Co^{III} in the PDECSZ as mentioned in the XRD analysis.

To search for a universal scaling behavior in the magnetization with field and temperature, the magnetization is represented versus H_{ef} /T in Fig.7 for all the isothermal curves for $T \geq$ 20K (above the transition temperature). The figure yields a universal behavior for each sample and clearly supports the assumption made in equation 2.

Each of these universal curves for every sample is fitted to a Langevin function, $L(x) = \coth(x) - \frac{1}{x}$, where $x = \frac{\mu_{ef} H_{ef}}{k_B T}$, and μ_{ef} is the average effective magnetic moment. The solid curve in Fig.7 shows this fit for the three coordinated polymers of Co^{II}, Co^{III} and Co^{II-III}, respectively. The average effective magnetic moments for the coordinated polymers, Co^{II}, Co^{III} and Co^{II-III} determined from the fit are 12.5μ_B, 10.3μ_B and 9.66μ_B, respectively, where μ_B is the Bohr magneton.

The molecular field values determined are about four orders of magnitude lower than that of cobalt atom, (H_m ~2100 T). However, the elemental Co is ferromagnetic, while the Co-doped samples are paramagnetic.

The effective magnetic moments for the three samples are approximately equal. This is higher than the corresponding magnetic moments of the Co-ions. Since the average magnetic moment of the Co^{II} is a little higher than for the other two samples, this reflects stronger exchange interaction in the Co^{II} coordinated polymer.



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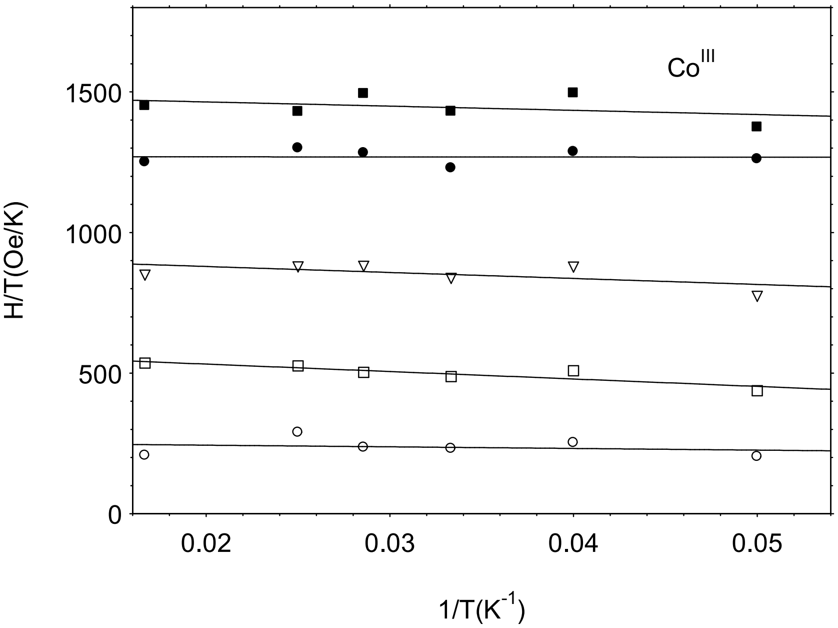

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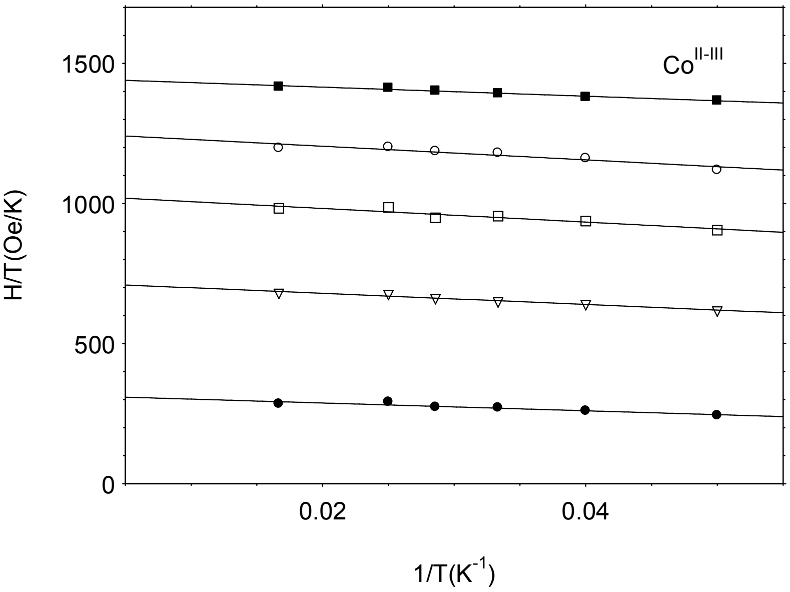
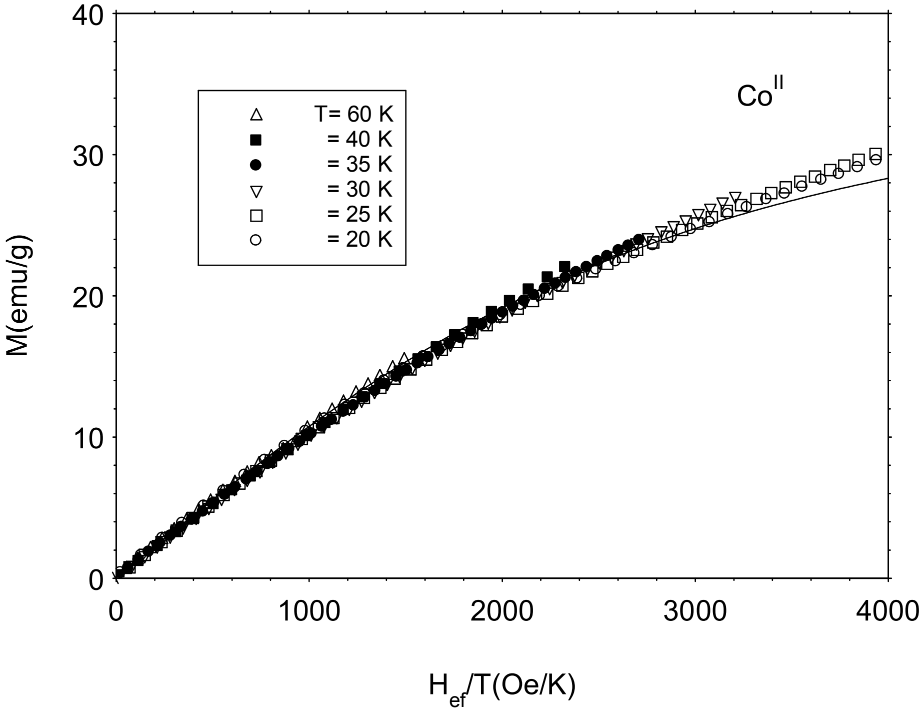
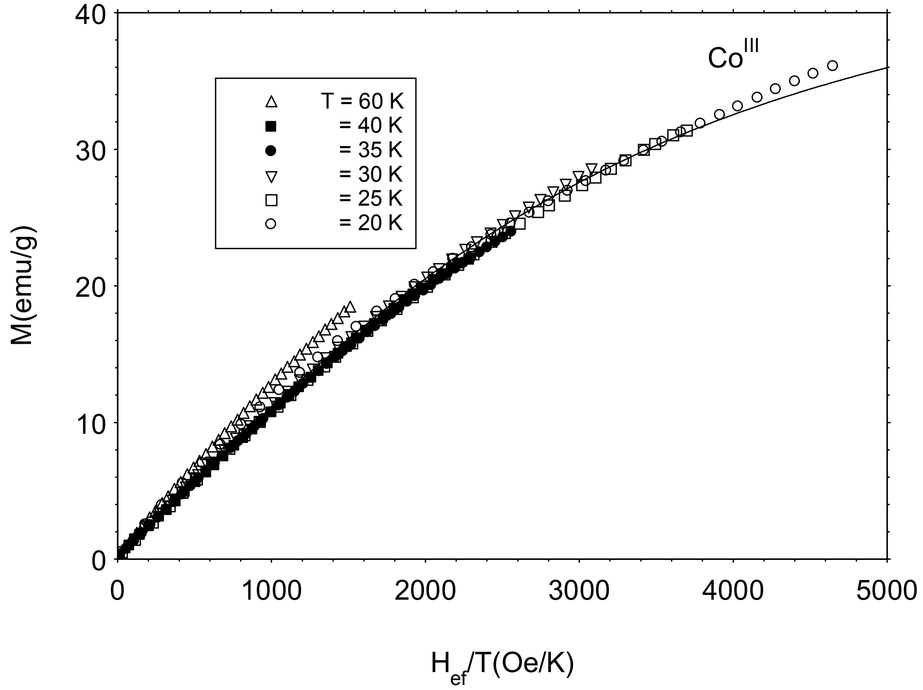


(c)

FIG. 6. Graph of H/T *versus* 1/T for the three samples of the Co-ions coordinated polymers (a) Co^{II}, (b) Co^{III} and (c) Co^{II-III} used to determine the average values of γ and H_m.



(a)



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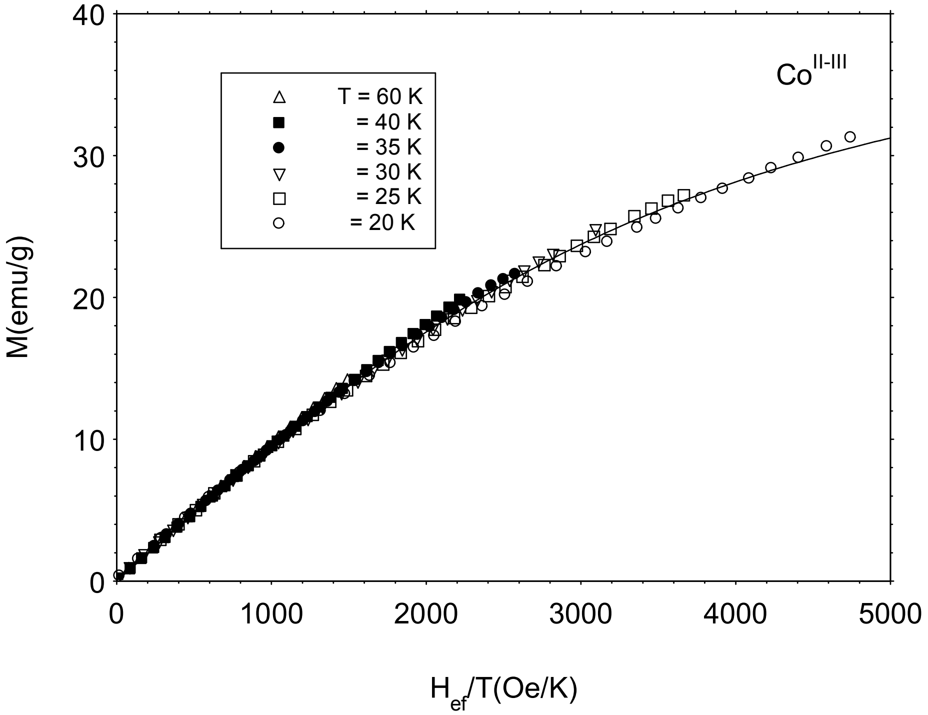

(c)

FIG. 7. Curves of M *versus* H_{ef}/T for $T \geq 20K$, where the solid line is the Langevin fit for the samples of the Co-ions coordinated polymers (a) Co^{II}, (b) Co^{III} and (c) Co^{II-III}.

Conclusions

From the above discussion, it can be concluded that Co^{II} coordinated polymer has a higher exchange interaction than the other two; namely Co^{III} and Co^{II-III}. It has been also found that the exchange interaction constant of the mixed valence polymer Co^{II-III} is nearly the difference between the values of the exchange interaction constants of Co^{II} and Co^{III}. Meanwhile, the molecular field of the mixed valence polymer is the sum of the corresponding values of the other two samples. This reflects the antifferimagnetic coupling of Co^{II} and Co^{III} in the Co^{II-III} sample. The mixed valence sample does not follow the simple additive rule.

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