Photoinduced Magnetism, Dynamics, and Cluster Glass Behavior of a Molecule-Based Magnet

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The dynamic susceptibility study of photoinduced magnetism in a molecule-based magnet, $K_{1-2x}Co_{1+x}[Fe(CN)_6] \cdot yH_2O$ ($0.2 \leq x \leq 0.4, y \sim 5$), is reported. Upon excitation with visible light the material has substantial changes in linear and nonlinear ac susceptibility and dc magnetization. The results demonstrate cooperative freezing of magnetic moments and absence of true long-range magnetic order. The ground and photoexcited states are described within a cluster glass model, with photoinduced increase in spin concentration leading to a shift of the dynamics to longer length and time scales and higher temperatures.

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The control of magnetic properties by light is an area of research that has attracted considerable attention in the recent years. Photoinduced changes in magnetic order were reported [1–6] in molecule-based magnets [7], as well as in magnetic semiconductor heterostructures [8] and manganite films [9]. Particularly interesting phenomena were reported for cobalt-iron Prussian blue analogs [1–4]. The reported photoinduced magnetization (PIM) effects include an increase in the ordering temperature, magnetization, remanent magnetization, and coercive field after illumination with red light. The photoinduced state is highly metastable and persists for several days at low temperatures [1]. The effect is erased by heating to $T \sim 150$ K and partially reversed by blue or near-infrared light [1,2]. The proposed origin of the effect is light-induced electron transfer from the state: $Fe^{II}(t_{2g}^6, S = 0)$-CN-$Co^{III}(t_{2g}^6, S = 0)$ to form the state: $Fe^{III}(t_{2g}^5, S = 1/2)$-CN-$Co^{II}(t_{2g}^5 e_g^2, S = 3/2)$ [1]. Thus increased spin concentration (n_s) is responsible for the observed magnetic transition. The reported theoretical [10–13] and experimental studies concentrated on the electronic transitions that cause PIM. However, no detailed study of the nature of magnetic ordering in the material has been reported. Earlier studies assumed [1–3] that this system exhibits long-range ferrimagnetic ordering below a well-defined critical temperature ($T_c \sim 16$ K). The chemical disorder (vacancies in Fe sites) is reported to be a factor that controls the occurrence and magnitude of the PIM effects (the PIM being absent in the $x = 0.5$ compound [3]), but effects of the disorder on the magnetic state have been ignored. We report here the first dynamic susceptibility study and the detailed dc magnetization properties of PIM in a Co-Fe Prussian blue analog, $K_{1-2x}Co_{1+x}[Fe(CN)_6] \cdot yH_2O$ ($0.2 \leq x \leq 0.4, y \sim 5$). Our results show that disorder in the system is sufficient to break the long-range magnetic order and cause glassy behavior. We present a new description of PIM effects, in terms of the light-induced changes in a cluster glass (CG).

The powders of $K_{1-2x}Co_{1+x}[Fe(CN)_6] \cdot yH_2O$ ($0.2 \leq x \leq 0.4, y \sim 5$) were synthesized following the procedure of Sato *et al.* [1]. The x-ray powder diffraction shows sharp Bragg peaks consistent with the fcc structure. The scanning electron microscopy (SEM) images show that the size of crystallites is in the range of $1-100$ μm. The samples for the study of PIM were prepared by encapsulating the powder in transparent nonmagnetic hosts. The linear and nonlinear ac susceptibility data were collected on a Lake Shore 7225 ac susceptometer, in zero applied dc magnetic field (H). The nonlinear susceptibilities χ_2 and χ_3 were measured by reading the $2f$ and $3f$ lock-in responses, respectively. The dc magnetization was measured with a quantum design SQUID magnetometer. Filtered light from a quartz-halogen lamp ($\lambda_{peak} = 650$ nm, FWHM $= 80$ nm) was used for illumination, the light being guided into the magnetometer/susceptometer by fiber guides. The measured intensity of light incident on the sample was $\sim 30-50$ mW/cm^2. Almost identical PIM is observed upon excitation by wavelengths between ~ 550 nm and ~ 750 nm, supporting that PIM is a broadband effect, rather than a resonant one.

The measured dc magnetization (M) of the ground (nonilluminated) and photoexcited states for the $x \approx 0.3$, $y \approx 4.6$ sample is displayed in Fig. 1. For the ground state, M rapidly increases as temperature is decreased below $T_c \approx 16$ K. The measurement of the temperature decay of remanence (M_{rem}) (measured after cooling in $H = 10$ Oe and subsequently reducing the field to zero) showed that M_{rem} vanishes (within the magnetometer's sensitivity) at ≈ 16 K. As T is further lowered below T_c, M exhibits strong irreversibility, given by the divergence of the field-cooled (M_{fc}) and zero-field-cooled (M_{zfc}) magnetization curves below a bifurcation temperature (T_{irr}). While for the lowest fields T_{irr} approaches T_c [inset (a), Fig. 1], the bifurcation is shifted to lower temperatures as H is increased. M_{zfc} exhibits a maximum at a field-dependent temperature $T_{max} < T_{irr}$. Strong irreversibility and shift of T_{irr} to lower T with increasing

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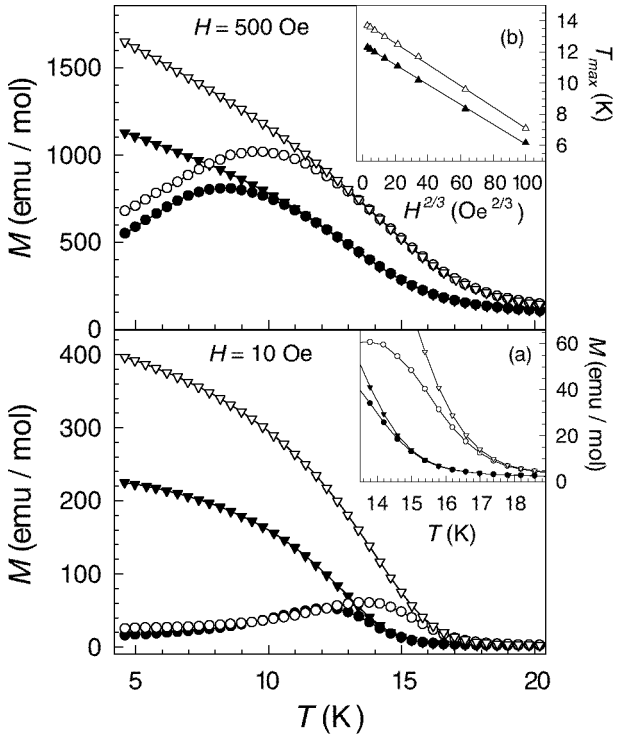

FIG. 1. $M_{\rm fc}$ (triangles) and $M_{\rm zfc}$ (circles) at $H = 10$ and 500 Oe for the ground and photoexcited states (solid and open symbols, respectively), for the $x \approx 0.3$, $y \approx 4.6$ sample. Inset (a): Enlargement near T_c for $H = 10$ Oe. Inset (b): Magnetic field dependence of the $M_{\rm zfc}$ peak temperature for the ground and photoexcited states (solid and open triangles, respectively), for 5 Oe $\leq H \leq$ 1000 Oe.

H are indications of glassy behavior [14,15]. However, while in canonical spin glasses (SG) the $M_{\rm fc}$ for T below $T_{\rm irr}$ levels off [14], in our data it monotonically increases with the lowering of T, similar to behavior of cluster glass materials [16–18]. The rapid rise in M at $\approx$16 K may be associated with the occurrence of finite range ferrimagnetic ordering, forming spin clusters near a quasicritical temperature T_c, the clusters becoming randomly frozen as T is further decreased (indicated by the peak in $M_{\rm zfc}$ at $T_{\rm max}$). After illumination M increases in the entire temperature region probed (below 30 K). The quasicritical temperature is increased to $T_c^{\rm illum} \approx 18.5$ K, as determined from the $M_{\rm rem}(T)$ data. The onset of irreversibility for the photoexcited state is immediately below $T_c^{\rm illum}$, similar to the data for the ground state. Inset (b) in Fig. 1 shows the $M_{\rm zfc}$ peak temperature $T_{\rm max}$ plotted versus $H^{2/3}$. A good linear fit is obtained for both the ground and photoexcited states, reminiscent of the Almeida-Thouless irreversibility line predicted by the mean-field theory (MFT) of spin glasses [14]. When data are fit with the triparameter functional form $T_{\rm max} = a - bH^{\delta}$, the δ values obtained are 0.63 ± 0.01 (0.69 ± 0.01) for the ground (photoexcited) state, very close to the expected MFT result of $\delta = 2/3$.

Figure 2 shows the time dependence of M, measured after zero-field cooling to 5 K and applying the field $H = 20$ Oe after a waiting period of $t_w = 3000$ s. After

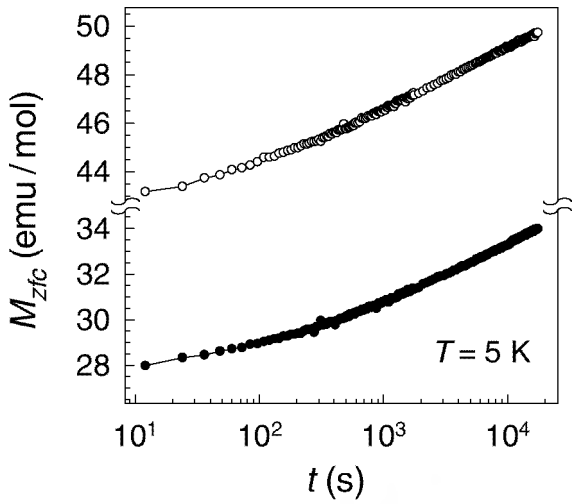

FIG. 2. Time dependence of $M_{\rm zfc}$ ($x \approx 0.3$ sample) for the ground and photoexcited states (solid and open symbols, respectively).

the field is applied (time $t = 0$), the magnetization exhibits a slow nonexponential increase, indicative of a nonequilibrium nature of $M_{\rm zfc}$. The long-time relaxation of the thermoremanent magnetization (TRM), measured after cooling in field and subsequently reducing the field to zero, also was recorded. The slow nonexponential relaxation of magnetization is another signature of glassiness [14]. Our data show no maximum in the relaxation rate S [$S \equiv dM_{\rm zfc}/d(\ln t)$] at $t = t_w$, in contrast with canonical SG [14], but similar to data reported for a CG [19].

The ac linear susceptibility ($\chi_{\rm ac} = \chi' - i\chi''$) for a frequency $f = 333$ Hz is displayed in Fig. 3. Both the in-phase (χ') and out-of-phase (χ'') susceptibilities exhibit peaks at T slightly above $T_{\rm max}$(10 Oe). The peaks systematically shift to higher T and decrease in height with increasing f (inset, Fig. 3). The frequency dependence of $\chi_{\rm ac}$ indicates slow relaxation processes that characterize the glassy behavior and freezing into a nonequilibrium state [14,20]. The relative shift of the χ' peak temperature T_p per decade of frequency is $\delta T_p \equiv (\Delta T_p/T_p)/\Delta(\log f) \approx 0.01$ in the ground state (decreased to $\approx$0.006 in the photoexcited state), a value characteristic for canonical spin glasses [14]. Both χ' and χ'' are increased by illumination and their peak temperatures increase by $\approx$2 K.

It is important to distinguish between the system studied here and a system of fine magnetic particles. The latter exhibits irreversible behavior below a f- and H-dependent blocking temperature T_b, related to the energy barriers induced by shape and crystalline anisotropies. For a system of noninteracting magnetic particles (superparamagnet, SP), the relative frequency variation of T_b is much larger than δT_p in our case, of the order of 0.1 [14]. The f dependence of T_b in a SP can be fit to the Arrhenius law for thermal activation over anisotropy barriers E_a, $\tau = \tau_0 \exp[E_a/k_B T_b]$, where $\tau = 1/f$ is the measuring time and τ_0 is the characteristic relaxation time. In the case of

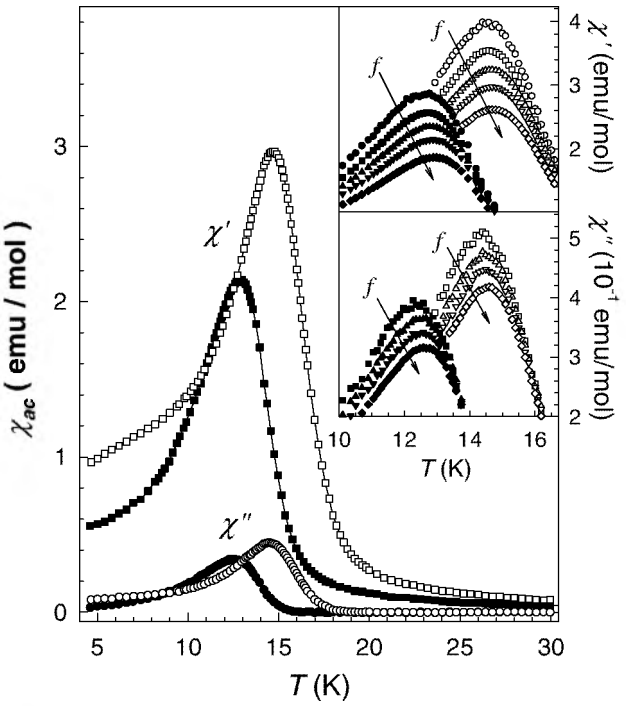

FIG. 3. Linear ac susceptibility ($x \approx 0.3$ sample) at ac field $H_{ac} = 1.4$ Oe and $f = 333$ Hz, for the ground and photoexcited states (solid and open symbols, respectively). Inset: χ' and χ'' for frequencies of 11 Hz (○), 33 Hz (□), 110 Hz (△), 333 Hz (▽), and 1100 Hz (◇) for the ground and photoexcited states (solid and open symbols, respectively).

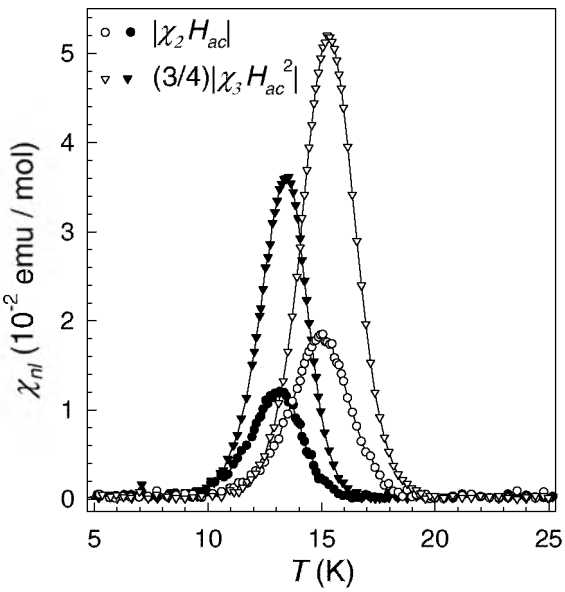

FIG. 4. Nonlinear ac susceptibility ($x \approx 0.3$ sample) at $H_{ac} = 15$ Oe, $f = 110$ Hz, for the ground and photoexcited states (solid and open symbols, respectively).

interacting particles, deviations from this law occur and better fit is obtained by using the Vogel-Fulcher (VF) law, $\tau = \tau_0 \exp[E_a/k_B(T_b - T_0)]$, where parameter T_0 is a measure of interparticle interaction strength. The value of the parameter $(T_b - T_0)/T_b$ is proposed as a criterion for distinguishing between different universality classes [21,22]. The VF law fit to our data gives reasonable values of parameters: for $\tau_0 = 10^{-13}$ s [23], $[T_p(11\text{ Hz}) - T_0]/T_p(11\text{ Hz}) \approx 0.12$ (0.07), $E_a \approx 42$ K (27 K), for the ground (photoexcited) state. The value of $(T_p - T_0)/T_p$ is in the range characteristic for canonical spin glasses [22,25]. In contrast, the Arrhenius law gives fit with unphysical values of parameters ($\tau_0 \sim 10^{-98}$ s, $E_a \sim 3000$ K for the ground state, $\tau_0 \sim 10^{-180}$ s, $E_a \sim 6000$ K for the photoexcited state).

The second (χ_2) and third (χ_3) harmonic susceptibilities (Fig. 4) exhibit relatively sharp peaks, suggesting divergence of these quantities. Both χ_2 and χ_3 are increased by illumination and their peak temperatures increased. One of the characteristic features of spin glasses is a divergence of the nonlinear susceptibility χ_3 at the freezing temperature, signifying a thermodynamic transition [14,26]. In contrast, in a system with progressive blocking of magnetic moments χ_3 is only weakly temperature dependent [27]. Thus both the two empirical criteria (the values of δT_p and $(T_p - T_0)/T_p$) and the behavior of χ_3 indicate a cooperative nature of the freezing process. The occurrence of χ_2 is inconsistent with the spin glass behavior and may be associated with the spontaneous magnetization within spin clusters.

We studied static and dynamic magnetic properties for several samples of Co-Fe Prussian blue with x in the range $0.2 \leq x \leq 0.4$. Figure 5 shows M for samples with $x \approx 0.2$, $y \approx 4.9$ and $x \approx 0.4$, $y \approx 6$. Both samples show strong irreversibilities with H-dependent bifurcation, similar to the $x \approx 0.3$ sample. Other characteristic CG features (slow relaxation of TRM and M_{zfc}, f-dependent χ_{ac} with δT_p of the order of 0.01, divergentlike peaks in harmonic susceptibilities) were also observed in all studied samples.

The experiments demonstrate that disorder in the system, while stabilizing PIM, brings about an unusual magnetic state with coexistence of phenomena related to magnetic order (large remanence and sharp increase of M below T_c, increase of M_{fc} below T_{irr}, occurrence of both χ_2 and χ_3) and glassiness (strong irreversibility with H-dependent bifurcation, long-time relaxation, frequency dependent χ_{ac}) for both the ground and photoexcited states. The results suggest that the infinite, percolating ferrimagnetic cluster, expected for fcc lattice with relatively high spin concentration [28], is broken into separate, yet strongly interacting clusters, likely due to the high level of chemical disorder (and, presumably, frustration). It was suggested [3,13] that the presence of Fe vacancies effects the spin state of the surrounding Co ions by lowering the crystal field, thereby favoring the high-spin state Co^{II}. Therefore the concentration of high-spin Co ions may be higher in the vicinity of vacancies, thus producing an inhomogeneous distribution of spins that favors the occurrence of clusters. The irreversible behavior of M occurs immediately below T_c, which suggests the onset of the progressive blocking of clusters for $T < T_c$. However, the behavior of linear and nonlinear ac susceptibility indicates

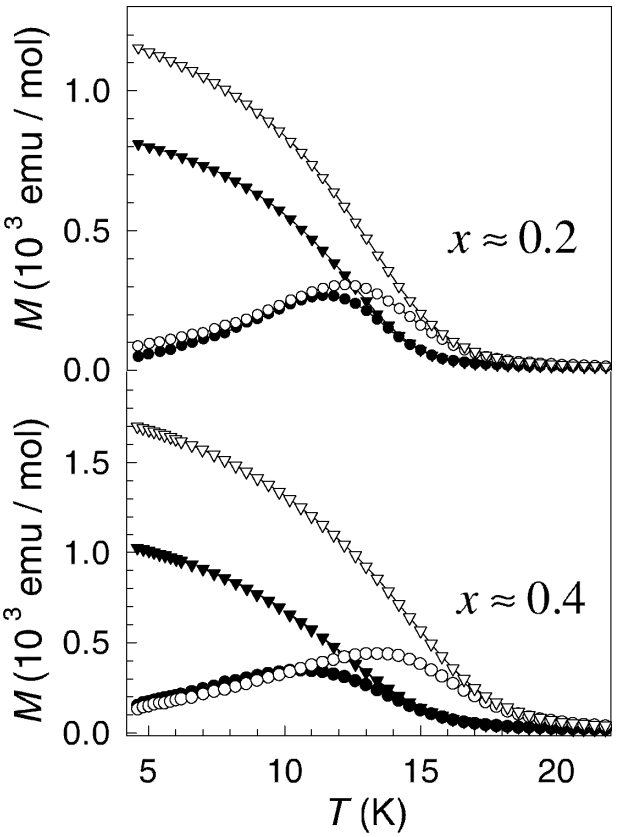

FIG. 5. $M_{\rm fc}$ (triangles) and $M_{\rm zfc}$ (circles) for the ground and photoexcited states (solid and open symbols, respectively) at $H = 50$ Oe, for samples with $x \approx 0.2$ and $x \approx 0.4$.

that, as the temperature is further lowered, cooperative freezing takes place at a temperature $T_g \equiv \lim_{f\to 0} T_p(f)$.

We propose that the static and dynamic magnetic behavior of the material is governed by the magnetization and dynamics of the spin clusters. As T_g is approached from above and temperature disorder decreased both the intracluster and intercluster interactions become more effective, and the sizes of clusters rapidly increase. Larger clusters are expected to have longer relaxation times (τ_r) [14], and thus freezing is followed by the growth of clusters and a shift of the distribution of τ_r to longer time scales. Starting from this simplified picture of the freezing process the observed behavior upon illumination can be qualitatively explained. It is suggested that as n_s in the photoexcited state is increased via photoinduced charge transfer, M within clusters is increased and, simultaneously, clusters grow in size. Since the distribution of cluster sizes in the photoexcited state is shifted to larger scales, so is the distribution of τ_r. Consequently, the slowing down of relaxation that characterizes freezing begins at a higher T than in the ground state. Also, due to the increased n_s, the formation of clusters occurs at a higher temperature $T_c^{\rm illum} > T_c$. The occurrence of glassiness in conjunction with PIM gives an interesting opportunity to study the evolution of magnetic order in a disordered magnet with an increase of n_s without changing the chemical composition of the sample. In particular, the observed decrease in δT_p upon illumination is a direct observation of the enhancement of intercluster magnetic correlations with increased n_s, in a single sample.

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