Cluster glass state and photoinduced effects on the freezing dynamics in $K_xCo[Fe(Cn)_6]_y \cdot zH_2O$ ($x \sim 0.16$, $y \sim 0.72$, $z \sim 4.4$)

D. A. Pejakovic[a)]
Department of Physics, The Ohio State University, Columbus, Ohio 43210

J. L. Manson and J. S. Miller
Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

A. J. Epstein
Department of Physics, The Ohio State University, Columbus, Ohio 43210

The magnetic properties and photoinduced magnetization of a Prussian blue analog, $K_xCo[Fe(Cn)_6]_y \cdot zH_2O$ ($x \sim 0.16$, $y \sim 0.72$, $z \sim 4.4$) were systematically studied. The frequency dependence of the linear ac susceptibility, the irreversibility in the field-cooled/zero-field-cooled magnetization (M_{FC}/M_{ZFC}), and the relaxation of M_{ZFC} suggest a cluster glass behavior. Illumination with red light leads to an increase in the magnetic irreversibility. While M_{FC} is significantly increased after illumination, M_{ZFC} at low temperatures is decreased. The observed photoinduced magnetic effects are explained within a cluster glass model. The photoinduced increase in the concentration of spins leads to a shift of dynamics toward longer length and time scales, resulting in freezing of spin clusters at a higher temperature. © *2000 American Institute of Physics.* [S0021-8979(00)18108-3]

I. INTRODUCTION

One of the interesting recent advances in the science of molecule-based magnetic materials[1] is the discovery of reversible photoinduced magnetization (PIM) in cobalt iron hexacyanide.[2,3] The reported photoinduced effects included an increase in the critical temperature (T_c) and in the field-cooled magnetization (M_{FC}), as well as an increase in magnetization in the paramagnetic region. This was accompanied by increased saturation magnetization, remanent magnetization, and coercive field. The PIM saturated after ~20 min of illumination with red light. The photoinduced effect persisted for several days at $T = 5$ K. The effect was erased by heating to $T \sim 150$ K, and partially reversed by blue or near-infrared light.

The suggested theoretical models[2,4–6] generally agree that PIM results from the light-induced charge transfer from the state: $Fe^{II}(t_{2g}^6, S=0)-CN-Co^{III}(t_{2g}^6, S=0)$ to the higher spin state: $Fe^{III}(t_{2g}^5, S=1/2)-CN-Co^{II}(t_{2g}^5 e_g^2, S=3/2)$. Increase in the number of spins leads to the increased magnetization and also, through the increase of number of magnetic neighbors, to the increase in T_c.[2]

Much of the earlier research concentrated on the dynamics of the electronic transitions that control switching from the low-spin to the high-spin state and vice versa. However, no detailed study of the nature of magnetic ordering in the material has been reported. We studied[7] in detail the ac susceptibility, the dc magnetization, and the PIM effect in the dc magnetization of (Co–Fe) hexacyanide, $K_xCo[Fe(Cn)_6]_y \cdot zH_2O$ ($x \sim 0.16$, $y \sim 0.72$, $z \sim 4.4$) While in earlier studies, it has been implied[2] that this system exhibits long-range ferrimagnetic ordering below a well-defined critical temperature $T_c = 16$ K, our results show behavior characteristic for cluster glasses (CG), with no true long-range order being present. Glassiness has profound effects on the dynamics of magnetic ordering, and requires a new formulation of the photoinduced magnetic effects.

II. EXPERIMENT

The powder sample of $K_xCo[Fe(Cn)_6]_y \cdot zH_2O$ ($x \sim 0.16$, $y \sim 0.72$, $z \sim 4.4$) was synthesized following the procedure of Sato *et al.*[2] The linear ac susceptibility was recorded on a Lake Shore 7225 susceptometer in zero dc applied field and in the temperature range of $4.4 \leqslant T \leqslant 30$ K on warming. Both the in-phase and out-of-phase susceptibilities were measured under an ac field $H_{ac} = 1.3$ Oe, in a wide range of frequencies ($11 \leqslant f \leqslant 11\,000$ Hz). The dc magnetization/PIM measurements were carried out with a Quantum Design SQUID magnetometer. The samples for PIM measurements were prepared by dispersing the powder in a thin layer on an adhesive tape. As a light source, a quartz-halogen lamp was used, the light being filtered by an interference filter ($\lambda_{peak} = 650$ nm, FWHM = 80 nm), and guided into the magnetometer by a fiber guide. The measured intensity of light incident on sample was ~35 mW/cm^2. Although during measurements samples were consecutively photoexcited and relaxed to the ground state (by heating above 150 K) several times, they did not show signs of aging or degradation, i.e., magnetization measurements were reproducible. The M_{FC} and M_{ZFC} data were taken as follows. The system was cooled in zero field to 4.6 K, field was turned on immediately after $T = 4.6$ K was reached, and data taken on warming from 4.6 to 30 K. The system was then cooled in field to 4.6 K and data taken again on warming to 30 K. The magnetization measurements for illuminated samples were performed after 1 h of illumination (enough to reach saturation of PIM) at $H = 0$ G and T

a)Electronic mail: pejakovi@mps.ohio-state.edu

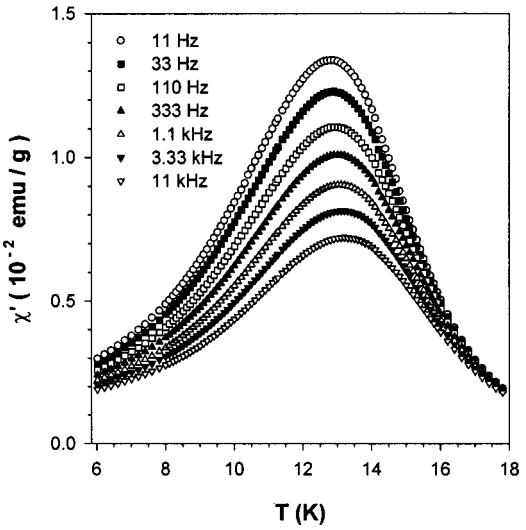

FIG. 1. In-phase linear susceptibility in $H_{ac}=1.3$ Oe (zero applied dc field) at frequencies between 11 Hz and 11 kHz.

$=5$ K. Before measurements, illuminated samples were warmed to 30 K, in order to erase the magnetic ordering, while preserving the effect of photoinduced change in the electronic state.

III. RESULTS AND DISCUSSION

The in-phase linear susceptibility (χ'), Fig. 1, exhibits a broad peak at a frequency-dependent temperature T_p. The peak height decreases with increasing frequency (f). This behavior is indicative of slow relaxation processes that characterize the glassy behavior and freezing into a nonequilibrium state at T_p.[8,9] The relative shift of T_p per decade of frequency (δT_p) is $\delta T_p \equiv (\Delta T_p/T_p)/\Delta(\log f) \approx 0.01$, a value characteristic for canonical spin glasses.[8]

The dc magnetization is displayed in Fig. 2. Below 16 K (18 K for illuminated sample) the magnetization rises rapidly with decreasing T. At lower temperatures M_{ZFC} deviates below M_{FC}, indicating history dependence of the magnetization processes. The bifurcation point (the temperature at which M_{FC} and M_{ZFC} curves merge) is shifted to lower temperatures as magnetic field (H) increases. Strong irreversibility, given by the difference between $M_{FC}(T)$ and $M_{ZFC}(T)$, and shift of the bifurcation point to lower T with the field increase reinforce the glassy behavior description.[8,10] While in usual spin glasses (SG) M_{FC} for T below the bifurcation point is almost flat,[8] in our data it continues to rise. Similar behavior has been reported for cluster glass (CG) materials.[11] The rapid rise in magnetization at about 16 K (18 K for illuminated sample) may be associated with the occurrence of the finite range antiferromagnetic coupling, forming clusters around a quasicritical temperature T_c. The peak in χ' may be attributed to the freezing of clusters as T is decreased below T_c. In the dc magnetization data, the freezing is indicated by the strong deviation between M_{FC} and M_{ZFC}, with a maximum in M_{ZFC} at a field-dependent temperature $T^{max}(H)$. As H is decreased, $T^{max}(H)$ approaches T_p for the lowest frequency used,[12] as expected for spin glass freezing.

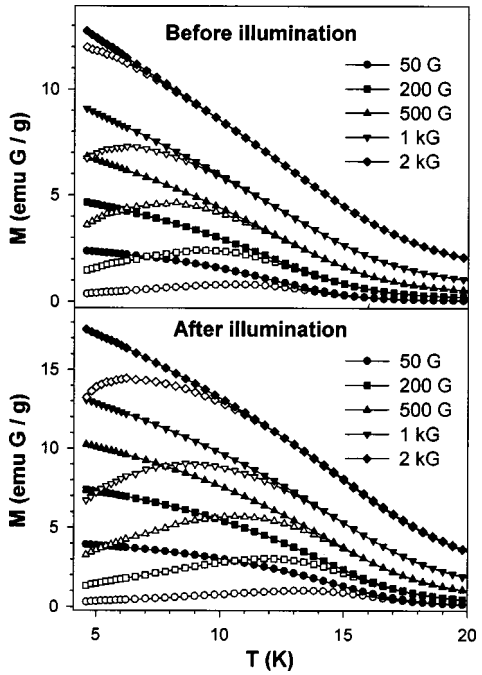

FIG. 2. Field-cooled (black symbols) and zero-field cooled (open symbols) magnetization before and after illumination as a function of temperature.

After illumination both T_c and $T^{max}(H)$ are increased (Fig. 2), indicating that formation of clusters and their freezing occur at higher temperatures. The irreversibility is more pronounced for illuminated sample, and persists even in the field of 0.2 T. The increase in irreversibility is more obvious in Fig. 3, where M_{FC} and M_{ZFC} for $H=100$ G are displayed. While M_{FC} is significantly increased by illumination ($\approx 57\%$), the $M_{ZFC}(T)$ curve for illuminated sample crosses over the $M_{ZFC}(T)$ curve for nonilluminated sample at $T \approx 9.5$ K, M_{ZFC} being slightly decreased after illumination. The point of crossover shifts to lower temperatures as field is increased and persists for fields up to 0.1 T, possibly for even higher fields at temperatures $T<4.6$ K.

The lomg-time relaxation of magnetization is another argument in favor of glassiness.[8,13] We detected relaxation of both M_{ZFC} (measured after cooling in zero field and applying the field after a waiting period t_w) and the thermoremanent magnetization (measured after cooling in field and subsequent reducing the field to zero). Figure 4 shows M_{ZFC} for

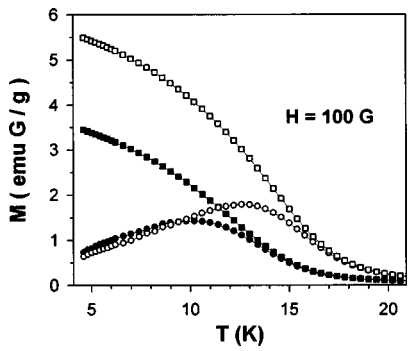

FIG. 3. M_{FC} and M_{ZFC} before (after) illumination [closed (open) symbols], at field of 100 G.

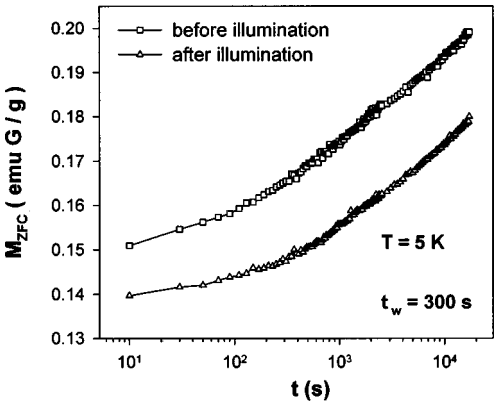

FIG. 4. Relaxation of M_{ZFC} at $T=5$ K and $H=20$ G, for a waiting time of 300 s.

$t_w=300$ s, $T=5$ K, and $H=20$ G. After the field is applied, the magnetization monotonically increases, indicative of a nonequilibrium nature of M_{ZFC}. For $t \gg t_w$ the data can be fit to a logarithmic time dependence.

We propose[7] that the magnetic state of the material is a cluster glass, with predominant antiferromagnetic coupling within clusters. For a system of noninteracting clusters (superparamagnet), δT_p is much larger than in our case, of the order of 0.1.[8] In contrast, small δT_p in our system indicates strong interaction among clusters and cooperative nature of the freezing process. The cluster size is characterized by the correlation length (ξ), which is for SG or CG always finite, but rapidly increases as temperature is decreased towards and below the freezing temperature.[8] Larger clusters have longer relaxation times (τ),[8] and thus the freezing process is followed by the growth of clusters and a shift of the distribution of τ toward longer time scales. Starting from this simplified picture of processes that occur in SG or CG around and below the freezing temperature, the observed behavior upon illumination can be qualitatively explained. It is suggested that as concentration of spins is increased via photoinduced charge transfer, the magnetization within clusters increases and, simultaneously, clusters grow in size (ξ increases). Since the distribution of cluster sizes shifts to larger scales, so does the distribution of τ. Consequently, the rapid increase in ξ and τ that characterizes the freezing process will begin at a higher temperature. Also, due to the increased spin concentration, the formation of clusters will occur at a higher temperature T_c.

The relative photoinduced increase in M_{FC} (δM_{FC})[14] is, for low magnetic fields, considerably larger than the relative increase in the number of spins (δN_s). We estimated[14] δN_s at $H=5.5$ T, where magnetization is almost saturated, and obtained $\delta N_s \leqslant 20\%$. However, δM_{FC} at lower fields (50–200 G) is as high as 65%. This is suggested to be a consequence of increased ordering within clusters and their more coherent response in field as the concentration of spins is increased by illumination. The photoinduced increase in irreversibility is thus a result of the two factors: enhanced coupling of spins within clusters (resulting in a large increase in M_{FC}), and enhanced freezing of clusters (leading to a decrease in the nonequilibrium magnetization M_{ZFC}).

In conclusion, our results suggest that $K_xCo[Fe(Cn)_6]_y \cdot zH_2O$ ($x\sim0.16$, $y\sim0.72$, $z\sim4.4$) exhibits a CG behavior, with only short-range order within clusters, and with strong interaction among clusters. The observed photoinduced phenomena are explained in a simple, yet coherent model, in which photoinduced increase in concentration of spins leads to the shift of dynamics toward longer length and time scales and higher temperatures.

ACKNOWLEDGMENTS

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[14] The quantity δM_{FC} is defined as $\delta M_{\mathrm{FC}}(\%) \equiv [(M_{\mathrm{FC}}^{\mathrm{illum}}/M_{\mathrm{FC}}^{0})-1] \times 100\%$, where M_{FC}^{0} ($M_{\mathrm{FC}}^{\mathrm{illum}}$) is M_{FC} before (after) illumination. Similarly, δN_s is defined as $\delta N_s(\%) \equiv [(N_s^{\mathrm{illum}}/N_s^{0})-1] \times 100\%$, where N_s^{0} (N_s^{illum}) is the number of spins before (after) illumination. We estimate δN_s as $\delta N_s(\%) \approx [(M_s^{\mathrm{illum}}/M_s^{0})-1] \times 100\%$, where M_s^{0} (M_s^{illum}) is the saturation magnetization before (after) illumination.