Evolution of Magnetic Polarons and Spin-Carrier Interactions through the Metal-Insulator Transition in $Eu_{1-x}Gd_xO$

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Raman scattering studies as functions of temperature, magnetic field, and Gd substitution are used to investigate the evolution of magnetic polarons and spin-carrier interactions through the metal-insulator transition in $Eu_{1-x}Gd_xO$. These studies reveal a spin-fluctuation-dominated paramagnetic (PM) regime for $T > T^* > T_C$, and a coexistence regime for $T < T^*$ in which spin polarons develop and coexist with remnants of the PM phase. They further show a strong connection between spin cluster formation and the dramatic field effects observed in these materials.

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Substantial recent evidence suggests that the remarkable phenomenon of "colossal magnetoresistance" (CMR) in perovskite-based oxides such as $La_{1-x}A_xMnO_3$, $La_{2-2x}A_{1+2x}Mn_2O_7$, and $La_{1-x}A_xCoO_3$ ($A = Sr, Ca$) [1] is associated with a tendency for these systems to be electronically inhomogeneous [2], due in part to a competition between different ordering tendencies. The ubiquity with which these dramatic phenomena are observed in perovskite-related magnetic systems raises questions as to whether similar "colossal" effects [2], spontaneous cluster formation, and electronic phase separation tendencies also influence a broader class of doped magnetic systems, e.g., ferromagnets such as EuO, EuS, and EuB_6, and antiferromagnets such as EuTe and EuSe [3,4]. Indeed, in addition to large negative magnetoresistivities near T_C, ferromagnetic Eu-based systems share many intriguing properties with higher T_C perovskite systems, including metal-insulator (MI) transitions accompanied by ferromagnetic-paramagnetic (FM-PM) phase changes near T_C, and evidence for magnetic cluster formation near T_C [5,6]. Consequently, these binary systems are particularly simple and well-controlled "laboratories" in which to explore the fundamental roots of spontaneous cluster development in doped magnetic systems, and to examine in particularly tractable systems the influence of disorder, magnetic field, etc., on cluster formation, "colossal" effects, and complex phase changes.

In this Letter, we present an inelastic light (Raman) scattering study of spin-carrier interactions and magnetic cluster (polaron) formation in the $Eu_{1-x}Gd_xO$ system [7,8] as functions of temperature, magnetic field, and Gd substitution. Raman scattering is a particularly effective technique for studying spin-carrier interactions in this system, as it affords a unique means of simultaneously investigating the carrier dynamics and spin excitations in various phases [5,6]. More particularly, spin-flip (SF) Raman scattering provides a sensitive and direct means by which FM clusters can be detected and studied in different phases of magnetic systems [5,6,9–12]. The Raman scattering study presented here provides clear spectroscopic evidence that, like the more complex perovskite-based magnetic oxides, the $Eu_{1-x}Gd_xO$ system exhibits a rich and dramatic variation in spectroscopic response as a function of temperature and magnetic field, including a regime in which magnetic clusters develop and coexist with regions characteristic of the PM regime. These studies reveal a connection between magnetic cluster formation and the "colossal" field effects observed in these systems; further, they allow us to examine the important effects of disorder and magnetic field on cluster formation.

Raman scattering measurements were performed with $Eu_{1-x}Gd_xO$ samples ($x = 0.006$: $T_C \sim 70$ K; $x = 0.035$: $T_C \sim 115$ K) mounted inside a continuous flow cryostat, which allowed Raman studies at temperatures ranging from 4 to 350 K, and in magnetic fields up to 8 T. Samples were excited in a backscattering geometry using the 647.1 nm excitation wavelength of a Kr-ion laser. For $H = 0$ measurements, linearly polarized light was employed in $z(xx)\bar{z}$ and $z(xy)\bar{z}$ configurations, where z and $\bar{z}$ represent the wave vector directions of the incident and scattered light, respectively, (x, y) represents the polarization directions of the incident and scattered light, respectively, and $x \parallel [1, 0, 0]$, $y \parallel [0, 1, 0]$, and $z \parallel [0, 0, 1]$. For $H \neq 0$ measurements, circularly polarized light was employed in a $z(LR)\bar{z}$ configuration, where L and R represent left and right circularly polarized light, respectively.

Conductivity measurements of EuO [7,8] can distinguish two distinct temperature regimes: a regime above T_C ($\sim$69 K) in which the resistivity exhibits activated behavior and a large negative magnetoresistivity, and a regime below T_C in which the conductivity increases by roughly 13 orders-of-magnitude as the system transitions into the FM metal phase. By contrast, as shown in Figs. 1(a) and 1(b), Raman scattering measurements resolve additional richness in the behavior of this system, revealing three temperature regimes with distinct spectroscopic signatures:

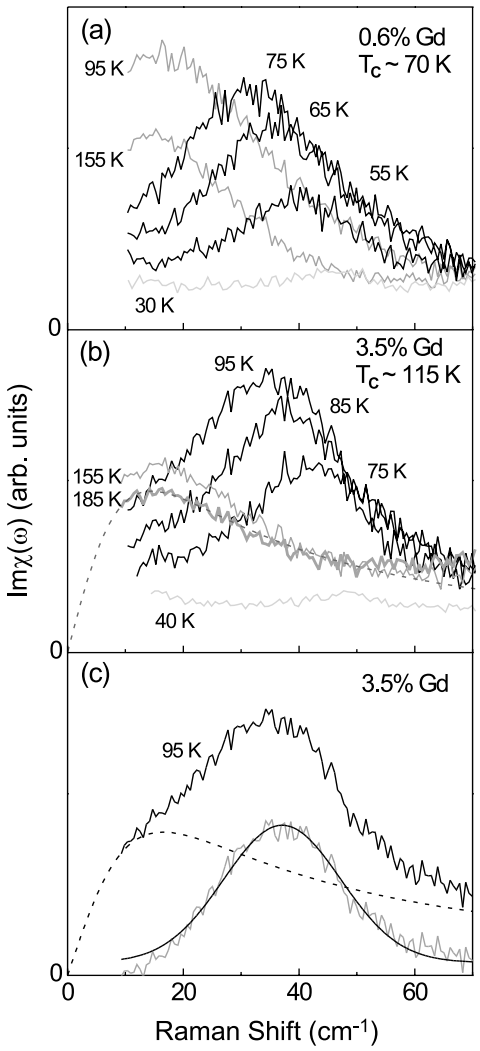

FIG. 1. Raman scattering spectra as a function of temperature for $Eu_{1-x}Gd_xO$ samples with (a) $x = 0.006$ and (b) $x = 0.035$. The dashed line in (b) indicates a fit to the Raman spectrum at 185 K using Eq. (1). (c) SF Raman response (bottom gray curve), which has been fit with a Gaussian profile (dark solid line), after removing the collision-dominated contribution (dashed line) from the raw $T = 95$ K spectrum (top curve).

(i) a high temperature "spin-fluctuation-dominated" PM regime for $T_C < T < T_{sf}$, where T_{sf} is the temperature below which carrier scattering is dominated by spin fluctuations, (ii) a "magnetic polaron" regime in which FM clusters develop below a formation temperature T^* ($T_C < T^* < T_{sf}$), and (iii) the FM regime for $T < T_C$, in which the FM clusters coalesce to form a FM metal phase.

The high temperature PM regime is characterized in the Raman spectrum by a collision-dominated electronic scattering response [5,6,13],

$$S(\omega) \propto [1 + n(\omega)]\,\mathrm{Im}\chi(\omega) = [1 + n(\omega)]\,\frac{|\gamma_L|^2 \omega \Gamma_L}{\omega^2 + \Gamma_L^2}, \tag{1}$$

where $1 + n(\omega)$ is the Bose thermal factor, L is the scattering channel selected by a particular scattering geometry, γ_L is the Raman scattering vertex in channel L, and Γ_L is the electronic scattering rate in channel L. Figure 1(b) illustrates that the collision-dominated response in Eq. (1) indeed provides an excellent fit (dashed line) to the Raman spectra in the PM phase. In conventional semiconductors, the scattering rate is typically associated with impurity scattering due to extrinsic defects or vacancies [14]. However, in magnetic semiconductors such as EuO and EuB_6, for temperatures sufficiently close to T_C, electronic scattering is dominated by short-range spin fluctuations. Consequently, we find in this regime that the scattering rate scales according to $\Gamma \sim \chi(T)T$ [6], where $\chi(T)$ is the temperature-dependent magnetic susceptibility. We also find that the intensity of the collision-dominated scattering response increases substantially with decreasing temperature towards T_C, mirroring the resistivity of $Eu_{1-x}Gd_xO$ [15] and further illustrating the dominance of "critical" electronic scattering from spin fluctuations throughout this temperature regime. However, the Raman results in Figs. 1(a) and 1(b) reveal additional complexity in the $H = 0$ behavior of $Eu_{1-x}Gd_xO$ as a function of temperature above T_C: below a temperature T^* ($> T_C$), there is a striking change in the Raman response, from a collision-dominated low frequency response to an inelastic response with a clear Gaussian profile. Significantly, this inelastic response develops in the (x, y) and $(x + y, x - y)$ (i.e., $E_i \perp E_s$) scattering geometries, but not in the (x, x) (i.e., $E_i \parallel E_s$) scattering geometry, and hence has the transformation properties of the totally antisymmetric Raman tensor. Previous investigations in both dilute and dense magnetic semiconductors have identified this distinctive response as $H = 0$ SF Raman scattering associated with the development of magnetic polarons [5,6,9–12]. Hence, the development of this Raman response in the $Eu_{1-x}Gd_xO$ system betrays a distinct regime above T_C in which local FM clusters nucleate prior to the development of the FM ground state. As a function of decreasing temperature below T^*, the energy of the $H = 0$ SF Raman response increases, reflecting an increase in the size and exchange energy ($\hbar\omega_0 \propto J_{df}\langle M\rangle$) of the magnetic clusters; moreover, the intensity of this SF response diminishes below T_C, reflecting the eventual coalescence of the magnetic clusters, and the consequent delocalization of charge, as the clusters evolve to form a FM metal phase.

Figures 1 and 2 reveal several important features of magnetic polaron evolution in $Eu_{1-x}Gd_xO$. First, the $H = 0$ SF Raman energy increases systematically with decreasing temperature, indicative of "cooperative" behavior, in which the spins of the carriers and magnetic ions are mutually aligned in the FM clusters [9,10,16]. Second, careful fits to the spectra, illustrated in Fig. 1(c) and summarized in Fig. 2, demonstrate that the magnetic polaron regime is characterized by the coexistence of $H = 0$ SF (inelastic Gaussian) and collision-dominated electronic [Eq. (1)] scattering responses, providing strong evidence that FM clusters coexist with some remnant of the PM phase in this temperature regime. This behavior is

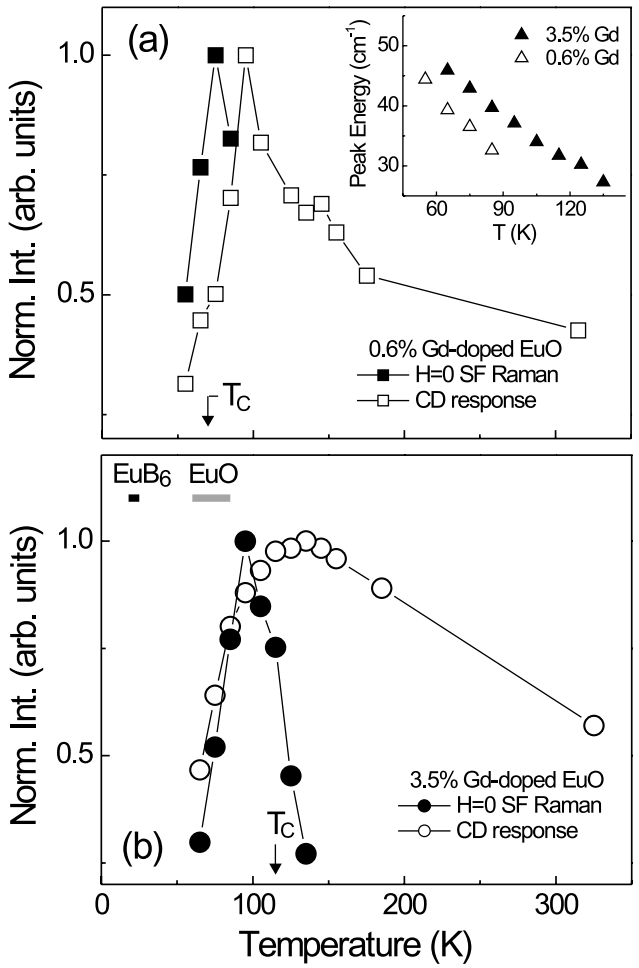

FIG. 2. Spectrally integrated intensity changes as a function of temperature both for the collision-dominated scattering response and for the magnetic polaron response in $Eu_{1-x}Gd_xO$ with (a) $x = 0.006$ and (b) $x = 0.035$. For comparison, the horizontal bars in (b) denote temperature ranges in which magnetic polarons form in EuO and EuB_6. The inset in (a) shows polaron peak energy changes as a function of temperature for $x = 0.006$ and 0.035.

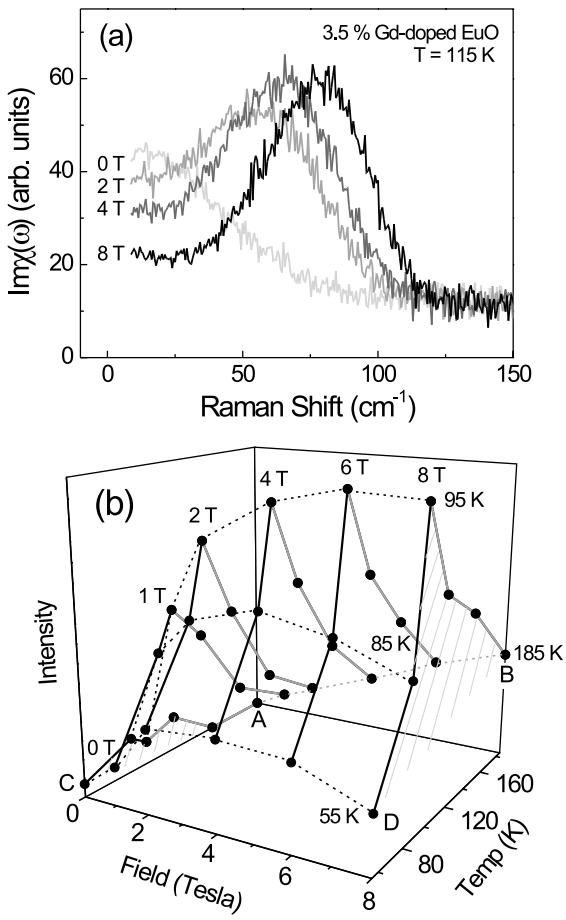

FIG. 3. (a) Magnetic field dependent Raman scattering at 115 K in the $z(LR)\bar{z}$ scattering configuration. (b) Spectrally integrated intensity profile of the SF Raman response as functions of magnetic field and temperature. Data points observed at the same field (temperature) are connected by the solid (dotted) lines.

summarized for both $x = 0.006$ and $x = 0.035$ samples in Fig. 2, which compares the integrated intensities of both the $H = 0$ SF (filled symbols) and collision-dominated scattering (open symbols) responses as a function of temperature. Finally, note that the polarons in $Eu_{1-x}Gd_xO$ are stable over a temperature range that is $\sim 5-10$ times higher than in EuB_6 [5,6]. Furthermore, both T^* and the temperature range over which polarons are stable increase with increasing Gd concentration, indicating that increasing disorder stabilizes magnetic clusters in CMR-type systems.

The field dependence of the Raman spectrum is illustrated for $T = 115$ K in Fig. 3(a), which shows the evolution of the SF Raman response with increasing magnetic field. The integrated intensity of the SF Raman response is summarized as functions of both the temperature and magnetic field in Fig. 3(b). Figures 3(a) and 3(b) show two particularly interesting effects of the magnetic field on the SF Raman spectrum in $Eu_{0.965}Gd_{0.035}O$. First, both the integrated intensity and the energy of the SF Raman response increase with increasing field, suggesting that there is a corresponding increase in the effective d-f exchange energy within the magnetic cluster. Second, the collision-dominated electronic response diminishes with increasing field, reflecting the decrease of spin fluctuations at high fields. The SF Raman intensity "surface" shown in Fig. 3(b) also reveals several features: (a) in the PM phase, increasing the magnetic field from $H = 0$ (i.e., from point A to B at $T = 185$ K) results in a roughly linear increase of the SF Raman intensity, suggesting that a magnetic field stabilizes the formation of magnetic polarons at high temperatures, presumably both by increasing the magnetic susceptibility, and by reducing the effects of thermal fluctuations; and (b) for $T < T_C$, increasing the magnetic field from $H = 0$ (e.g., from point C to D at $T = 55$ K) causes the SF Raman intensity to increase initially at lower fields, then decrease for higher fields, suggesting that at sufficiently high fields and/or low temperatures, the system is close to the FM metal phase boundary at which the magnetic clusters percolate and the carriers delocalize.

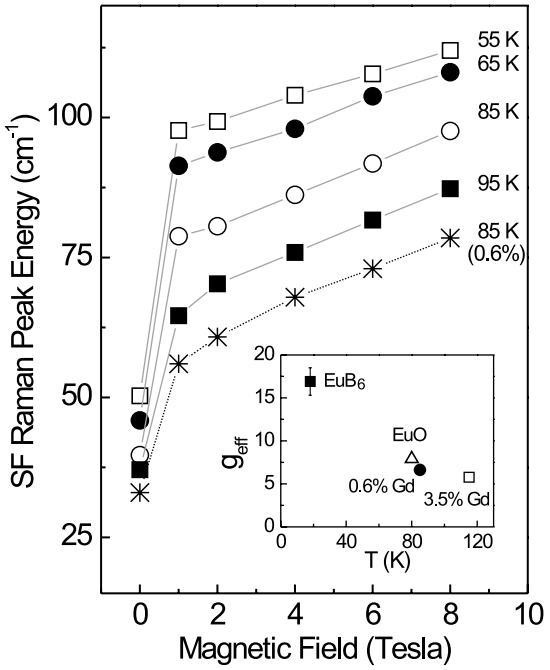

FIG. 4. SF Raman peak energy as a function of applied magnetic field at various temperatures for $Eu_{1-x}Gd_xO$ with $x = 0.006$ (stars) and 0.035 (squares and circles). The inset shows the effective g value ($\sim \Delta E/\mu_B \Delta H$) obtained from linear fits in the field range of $1 \leq H \leq 8$ T.

In order to examine more quantitatively the effects of a magnetic field on the magnetic polarons in $Eu_{1-x}Gd_xO$, we plot in Fig. 4 the SF Raman energy as a function of field at several temperatures for both 0.6% Gd- (stars) and 3.5% Gd- (squares and circles) substituted EuO. To simplify the interpretation of these data, we consider only field-dependent data at those temperatures for which there is an $H = 0$ SF Raman response, i.e., for which there are magnetic polarons at $H = 0$. The summary in Fig. 4 illustrates several interesting points. First, there is an abrupt jump in the SF Raman peak energy between 0–1 T, followed by a linear increase in the SF energy with increasing magnetic field. As the SF Raman energy is given by $\hbar\omega_0 \propto J_{df}\langle M\rangle$, the increase with increasing field indicates an abrupt enhancement in the exchange energy associated with the polarons for relatively small fields. This may reflect a rapid enhancement in the effective field experienced by localized charges when the magnetic clusters—which are randomly oriented at $H = 0$—become mutually aligned by a small field. Second, Fig. 4 illustrates that the SF Raman energy increases both with decreasing temperature and with increasing Gd concentration, again presumably reflecting the larger effective magnetization associated with the polarons under these conditions [2,17]. Using the slope obtained from the linear-in-field "high-field" regime ($1 \leq H \leq 8$ T), we can estimate an effective g value g_{eff} ($\sim \Delta E/\mu_B \Delta H$) of ~ 6 for both 0.6% and 3.5% (Eu,Gd)O at $T \sim T_C$. By contrast, the much less disordered system EuB_6 has $g_{\text{eff}} \sim 17$, suggesting that disorder significantly depresses the rate at which clusters evolve with field. Yet these results also indicate that the development and presence of spin clusters strongly amplify the effects of a magnetic field on the electronic properties of these systems: first, by generating huge effective fields "seen" by the carriers, the strengths of which dramatically increase with field due to the large g_{eff} values; and second, through the field-induced percolation of clusters, which should be dramatically manifest in the conductivity.

In summary, Raman scattering studies reveal direct evidence for several diverse temperature regimes in $Eu_{1-x}Gd_xO$, most notably a coexistence regime in the vicinity of T_C involving the presence of both FM clusters and remnants of the high temperature PM phase. This interesting magnetic cluster regime is found to be stabilized both by magnetic field and disorder. Importantly, our results demonstrate the strong connection between spin cluster development and the large field-induced effects observed in these materials; further, they show that spontaneous cluster formation near T_C is not unique to complex oxides such as the manganites, but occurs even in structurally simple systems that exhibit a similar competition among carrier kinetic, Coulombic, and magnetic exchange energies.

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