Evolution of magnetic polarons and spin-carrier interactions through the metal-insulator transition in Eu$_{1-x}$Gd$_x$O

H. Rho,$^1$ C. S. Snow,$^1$ S. L. Cooper,$^1$ Z. Fisk,$^2$ A. Comment,$^1,3$ and J-Ph Ansermet$^{1,3}$

$^1$Department of Physics and Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801
$^2$National High Magnetic Field Laboratory, Florida State University, 1800 East Paul Dirac Drive, Tallahassee, Florida 32306
$^3$Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

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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$_x$O. These studies reveal a greater richness of phase behavior than have been previously observed using transport measurements: a spin-fluctuation-dominated paramagnetic (PM) phase regime for $T>T^*$, a two-phase regime for $T<T^*$ in which magnetic polarons develop and coexist with a remnant of the PM phase, and an inhomogeneous ferromagnetic phase regime for $T<T_C$.

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The remarkable phenomenon of “colossal magnetoresistance” (CMR) in perovskite-based oxides such as La$_{1-x}$A$_x$MnO$_3$, La$_{2-2x}$A$_{1+2x}$Mn$_2$O$_7$, and La$_{1-x}$A$_x$CoO$_3$ (A = Sr, Ca) has renewed interest in the Eu-based systems [1]. EuO, EuS, and EuB$_2$O$_4$ are paramagnetic (PM) phase regime for $T>T_C$, a two-phase regime for $T<T_C$ in which magnetic polarons develop and coexist with a remnant of the PM phase, and an inhomogeneous ferromagnetic phase regime for $T<T_C$.

The Eu$_{1-x}$Gd$_x$O system is particularly interesting to study for several reasons. Conductivity and magnetic susceptibility measurements have shown that Eu-rich EuO exhibits a FM-PM phase change near $T_C$ of $69$ K [3, 4], affording an opportunity to investigate spectroscopically the nature of transitions between various complex phases as functions of temperature and magnetic field. Furthermore, substitution of Gd provides a means of elevating both $T_C$ [5] and the conductivity [6] in a systematic and controlled manner, enabling one to study the effects of both $T_C$ and disorder on spin-carrier interactions and magnetic polaron formation.

In this Letter, we present an inelastic light (Raman) scattering study of spin-carrier interactions and magnetic polaron formation in the Eu$_{1-x}$Gd$_x$O system as functions of temperature, magnetic field, and Gd substitution. Raman scattering is a particularly effective technique for studying spin-carrier interactions in magnetic systems, as it affords a unique means of simultaneously investigating both the carrier dynamics and spin excitations in various phases of these materials [8, 9]. More particularly, spin-flip (SF) Raman scattering provides a sensitive and direct means by which magnetic polarons can be detected and studied in different phases of magnetic semiconductors [8, 9, 10, 11, 12, 13].

Raman scattering measurements were performed with Eu$_{1-x}$Gd$_x$O samples ($x=0.006$; $T_C ≈ 70$ K; $x=0.035$; $T_C ≈ 115$ K) mounted inside a variable-temperature, continuous helium-flow cryostat, which allowed Raman studies at temperatures ranging from 4K to 350K, and in magnetic fields up to 8T. Samples were excited in a true-backscattering geometry using the 647.1 nm excitation wavelength of a Kr-ion laser. For $H=0$ measurements, linearly polarized light was employed in $z(xy)\parallel z$ and $z(xy)\parallel z$ configurations, where $x\parallel [1,0,0]$, $y\parallel [0,1,0]$, and $z\parallel [0,0,1]$. In the notation $z(xy)\parallel z$, $z$ and $\bar{z}$ represent the wavevector directions of the incident and scattered light, respectively, and $(x,y)$ represents the polarization directions of the incident
Collision-dominated contribution (dashed line) from the raw fit with a Gaussian profile (dark solid line), after removing (c) SF Raman response (bottom gray curve), which has been employed in a regime above \( T > T_C \). For magnetic field \( T = 95 \) K spectrum (top curve).

The high temperature PM phase is characterized in the Raman spectrum by a collision-dominated electronic scattering response \( S(\omega) \propto (1 + n(\omega))Im\chi(\omega) = (1 + n(\omega))\frac{|\gamma_L|^2 \omega \Gamma_L}{\omega^2 + \Gamma_L^2}, \) (1)

where \( 1 + n(\omega) \) is the Bose thermal factor, \( L \) is the scattering channel selected by a particular scattering geometry, \( \gamma_L \) is the Raman scattering vertex in channel \( L \), and \( \Gamma_L \) is the electronic scattering rate in channel \( L \). Fig. 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 \([13]\). 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 \( \Gamma \propto \chi(T)T \) \([14]\), where \( \chi(T) \) is the temperature-dependent magnetic susceptibility, and we also find that the intensity of the collision-dominated scattering response increases substantially with decreasing temperature towards \( T_C \). Significantly, the resistivity of Eu\(_{1-x}\)Gd\(_{x}\)O \([10]\) exhibits activated behavior between room temperature and \( T_C \), which also suggests the dominance of “critical” electronic scattering from spin fluctuations throughout this temperature regime. However, the Raman results in Fig. 1(a) and (b) reveal additional complexity in the \( H = 0 \) phase behavior of Eu\(_{1-x}\)Gd\(_{x}\)O 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., \( E_\parallel \perp E_\parallel \)] scattering geometries, but not in the \( (x, z) \) [i.e., \( E_\parallel \parallel E_\parallel \)] scattering geometry, and hence has the transformation properties of the totally antisymmetric Raman tensor. Numerous 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 \([13, 14, 11, 12, 13, 13]\). Hence, the development of this Raman response in the Eu\(_{1-x}\)Gd\(_x\)O 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 \( T_C \), the \( H = 0 \) SF Raman
FIG. 2: Spectrally integrated intensity changes as a function of temperature both for collision-dominated scattering response and for magnetic polaron response in Eu$_{1-x}$Gd$_x$O with (a) $x = 0.006$ and (b) $x = 0.035$. Horizontal bars in (b) denote temperature ranges in which magnetic polarons form in EuO and EuB$_6$ for a comparison purpose. The inset in (a) shows polaron peak energy changes as a function of temperature for $x = 0.006$ and 0.035.

response gradually decreases in intensity as the system transitions into the FM metal phase, reflecting the gradual dissolution of localized magnetic polarons with increasing spin order in the FM phase as the localization length for the magnetic polarons diverges. Below 50 K, the Raman intensity associated with magnetic polarons decreases rapidly due to the saturation of spins.

Figures 1 and 2 reveal several important features of magnetic polaron evolution in Eu$_{1-x}$Gd$_x$O. First, the H = 0 SF Raman energy increases systematically with decreasing temperature, indicative of magnetic polarons in a spin-aligned “cooperative” regime, in which the spins of the carriers and magnetic ions are cooperatively aligned in the FM clusters.[10, 11, 17]. 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 this is a “two-phase” regime in which FM clusters coexist with some remnant of the PM phase. This behavior is 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$_x$O are stable over a temperature range that is $\sim 5$–10 times higher than in EuB$_6$.[8, 9]. Furthermore, both $T^*$ and the temperature range over which polarons are stable increase with increasing Gd-concentration. These results provide direct evidence that increased spin-disorder stabilizes magnetic polarons in the CMR-type systems.

It is of great interest to examine the effects of an externally applied field on the low frequency excitation spectra near $T_C$ in Eu-based compounds, and more particularly on the magnetic polarons in these systems. The field dependence of the Raman spectrum is illustrated for $T = 115$ K in Fig. 3 (a), which shows the evolution of a 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 (b) show two particularly interesting effects of the magnetic field on the SF Raman spectrum in Eu$_{1-x}$Gd$_x$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 the development and linear increase in the SF Raman intensity, suggesting that a magnetic field stabilizes the formation of magnetic polarons at high temperature, presumably by both increasing the magnetic susceptibility at these
Fig. 4 illustrates that the SF Raman energy increases mutually-aligned with the application of a field. Second, by localized charges when the magnetic polarons become randomly oriented at $H = 0$, but are expected to become dominant at $T \sim T_C$. By contrast, the much less disordered system EuB$_6$ has $g_{eff} \sim 17$ for $T \sim T_C$, suggesting that the polaron size in (Eu,Gd)O may be fundamentally much more limited by intrinsic spin disorder than in EuB$_6$. Indeed, the PM semimetal to FM metal transition in EuB$_6$ appears to occur via a continuous evolution — and eventual percolation — of the magnetic polarons, whereas the polaronic SF Raman response in (Eu,Gd)O simply appears to dissipate into the FM phase (see Fig. 3(b)) with decreasing temperature.

In summary, Raman scattering studies reveal direct evidence for diverse phase behavior in Eu$_{1-x}$Gd$_x$O, most notably a coexistence regime involving magnetic polarons and PM phase regions in the vicinity of $T_C$. This regime is found to be stabilized both by increasing magnetic field and the substitution of magnetic impurities. These results demonstrate, most significantly, that electronic inhomogeneity and cluster formation are not unique to complex, perovskite-related oxides, but occur rather generally even in structurally simple (binary) systems that exhibit a similar strong competition between carrier kinetic and magnetic interaction energies.

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