Magnetic polaron effect in $Sr_{8-x}Eu_xGa_{16}Ge_{30}$ clathrates probed by electron spin resonance

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(Received 15 November 2012; revised manuscript received 17 April 2013; published 14 June 2013)

Single crystals of the type-I clathrate series $Sr_{8-x}Eu_xGa_{16}Ge_{30}$ ($x = 0.01$–8) were grown by Ga flux and systematically studied by magnetic susceptibility, electrical resistivity, and electron spin resonance (ESR) measurements. Both magnetic transition temperatures (T_c and T^*) were mapped as a function of x. We found that the Curie temperature (T_c) and the magnetic anomaly temperature (T^*) decrease systematically as Eu is substituted by Sr until no ordering is observed above 2 K for $x = 1.0$. For samples where the rattling Einstein temperature of $\theta_E \approx 25$–60 K lies above T_c, we have observed no features in the ESR data, suggesting that the Eu^{2+} $4f$ spin dynamics is weakly coupled to the rattling modes. As the temperature is lowered and the magnetic field is increased, the ESR linewidth (ΔH) behavior points to the formation of magnetic polarons.

DOI: 10.1103/PhysRevB.87.224414 PACS number(s): 76.30.−v, 71.38.−k

I. INTRODUCTION

In most materials, electrical and thermal conductivity go hand in hand. Consequently, the dimensionless figure of merit for thermoelectricity, ZT, is small ($ZT \ll 1$, where T is the temperature, $Z = S^2\sigma/\kappa$, S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity). Thus practical thermoelectrical applications, such as refrigeration and energy saving, are not viable. However, Slack suggested that *phonon glass-electron crystals* (PGECs) with a large Seebeck coefficient are likely to be very good thermoelectric materials. PGEC materials have the shortest (largest) possible phonon (electron) mean free path and one should look for them in ternary semiconducting compounds, A_xBC_y, where B atoms undergo large local anharmonic vibrations (or "rattling") that do not disturb the conduction electrons (ce) in the conducting framework $A + C$.[1]

Following this approach, clathrate compounds are promising thermoelectric materials.[2–4] With the general formula $A_xM_yX_{46-y}$, clathrates are periodic solids in which atoms, ions, or molecules of one component (guest A) are physically trapped within the crystal structure of another ($[M_yX_{46-y}]$ cage). The guest atoms interact weakly with the covalent tetrahedrally bonded cages. Therefore, the guest "rattles" inside the oversized cages and efficiently scatters heat-carrying phonons.

Among the existing clathrates, the type-I $A_8Ga_{16}Ge_{30}$ has been extensively studied recently.[5–9] This compound crystallizes in the $Pm\bar{3}n$ structure, which contains Ga-Ge atoms arranged in two E_{20} pentagonal dodecahedra and six E_{24} tetrakaidecahedra cages that host two $A(1)$ atoms at the $2a$ site and six $A(2)$ atoms at the $6d$ site, respectively. The $A(2)$ ions in the tetrakaidecahedra have been found to deviate from the centered $6d$ site, in favor of fourfold split, off-centered $24k$ sites. The off-center and strongly anharmonic vibration of the $A(2)$ ions leads to an even greater enhancement of phonon scattering.[10,11]

In particular, one interesting guest ion is the magnetic divalent europium. $Eu_8Ga_{16}Ge_{30}$ is the only known clathrate in which the guest atoms are fully occupied by magnetic ions and that also might be suitable for thermomagnetic applications. Besides its relatively high thermopower, high electrical conductivity, and very low thermal conductivity, this compound exhibits a ferromagnetic transition at $T_c = 35$ K, followed by a secondary magnetic anomaly at $T^* = 23$ K.[11–17] The shortest Eu-Eu distances in this compound are Eu(2)-Eu(2) = 5.23 Å, Eu(2)-Eu(1) = 5.62 Å, and Eu(1)-Eu(1) = 10.7 Å. Due to the weak bonding and the large separation between Eu spins, the magnetic ordering arises from Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction between the local Eu^{2+} $4f$ moments via ce.[18,19]

ESR is a highly sensitive technique used to study spin fluctuations and magnetic interactions in a variety of compounds. In particular, the crystal electric-field (CEF) effect is a higher order effect in the Eu^{2+} S-state ($S = 7/2$, $L = 0$) ground state. As such, they are excellent ESR probes to study magnetic properties which purely reflect the details of RKKY magnetic interaction and Fermi-surface effects in intermetallic magnetic materials. These studies can reveal details about the microscopic interaction J_{fs} between the $4f$ electrons and the ce. Therefore, the main goal of the present work is to further investigate the microscopic details of the Eu^{2+}-Eu^{2+} magnetic interactions and their coupling with the electronic and charge degrees of freedom in the host compound.

It has been proposed that the EuM_4Sb_{12} (M = Fe, Ru, Os) skutterudites have a unique behavior of the ESR spectra (i.e., a broad maximum of the linewidth ΔH near θ_E) due to the coupling between the rattling modes and the electronic degrees of freedom leading to a spin-glass-type spin dynamics. However, no comparable phenomenon is observed in the clathrate compound. In fact, in this case, the measured g shift, $\Delta g = g_{\text{experiment}} - g_{\text{insulator}} \approx 0.005(4)$, gives, in the simplest scenario of a single-band metal, approximately the measured Korringa rate (i.e., the slope of the ΔH linear increase with increasing temperature), $b \approx 0.8$ Oe/K, suggesting a $\mathbf{q}$-independent J_{fs} and the absence of multiband effects.[20,21]

On the other hand, it was conjectured that in the $Eu_8Ga_{16}Ge_{30}$ compound, a spin-glass-like behavior below θ_E may be prevented from occurring by the magnetically ordered state.[20] In this work, we show that for samples where the rattling Einstein temperature θ_E lies above the ordering temperature, we still do not observe a broad maximum in the T-dependent ESR linewidth. In contrast, the

Eu^{2+} spin dynamics is dominated by the formation of magnetic polarons. For completeness, we also performed transport and magnetic measurements to characterize the samples studied by ESR. This allowed us to obtain the phase diagram of the $Sr_{8-x}Eu_xGa_{16}Ge_{30}$ series.

II. EXPERIMENTAL DETAILS

All single crystalline samples of the intermetallic $Sr_{8-x}Eu_xGa_{16}Ge_{30}$ series were grown at UNICAMP (Brazil) using the Ga-flux technique with starting composition $Sr:Eu:Ga:Ge = (8-x):x:38:30$ with $x = 0.01$, 0.04, 0.4, 1.0, 2.0, 4.0, 6.0, 8.0. The flux was removed by centrifugation after the thermal treatment. The crystal structure and phase purity were determined by x-ray powder diffraction in a Bruker D8 Powder Diffractometer. The in-plane resistivity was measured using a standard four-probe method. Magnetization measurements were made using a superconducting quantum interference device (SQUID) magnetometer, MPMS5 (Quantum Design). ESR measurements were performed in a BRUKER spectrometer equipped with a continuous He gas-flow cryostat. *X*-band ($\nu = 9.49$ GHz) and *Q*-band frequencies ($\nu = 34$ GHz) were used in the temperature region $4.2 < T < 300$ K. The ESR samples were prepared as platelets with well-defined faces and the experiments were performed with the applied field perpendicular and parallel to a particular crystallographic direction.

III. RESULTS AND DISCUSSION

To better illustrate the evolution of the physical properties along the series, we present the data of four representative Eu concentrations. The temperature dependence of the in-plane normalized electrical resistivity from 300 to 2 K is shown in Fig. 1(a). The room-T and the residual resistivity ratio (RRR) values vary in the range 2–22 mΩ cm and 0.9–1.3, respectively. A metallic behavior is observed in the paramagnetic regime. At low temperatures, a sharp peak appears at $T_c = 25$ K and a broader peak appears at $T^* = 13$ K for $x = 6.0$. For $x = 2.0$,

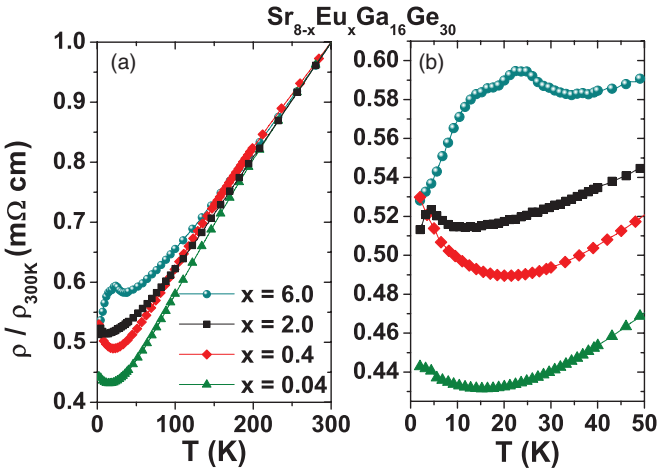

FIG. 1. (Color online) (a) Temperature dependence of electrical in-plane resistivity normalized to the room-temperature value for $Sr_{8-x}Eu_xGa_{16}Ge_{30}$. (b) Low-temperature resistivity showing the peaks associated with T_c and T^*.

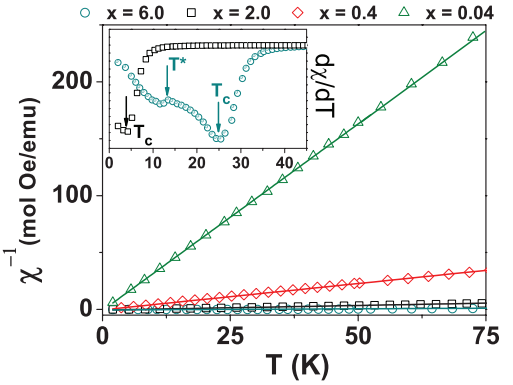

FIG. 2. (Color online) Magnetic susceptibility inverse as a function of temperature taken at low applied magnetic field $H = 1$ kOe. The inset shows the first derivative of χ, and both T_c and T^* are indicated by arrows.

only the sharp peak at $T_c = 4$ K is observed, and for $x \leqslant 1$ and T > 2 K, no transition is observed.

The ferromagnetic sharp peak resembles the behavior observed for EuB_6 single crystals, where the presence of magnetic polarons dominates the electron scattering near the ferromagnetic transition.[22]

Figure 2 displays the magnetic susceptibility inverse as a function of temperature taken at the applied magnetic field of $H = 1$ kOe. For all x values in the $Sr_{8-x}Eu_xGa_{16}Ge_{30}$ series, $\chi^{-1}(T)$ show a Curie-Weiss (linear) behavior for $T > T_c$. At low T and $x \geqslant 2$, we observe a ferromagnetic transition that is followed by a second magnetic transition for $x > 2$. Both magnetic transitions are clearly visible in the magnetic susceptibility derivative (inset of Fig. 2).

From the linear fits for $T > T_c$ (solid lines in Fig. 2), we obtained both Curie-Weiss temperature θ_{CW} (27, 7, 0.7, and 0.04 K for $x = 6.0, 2.0, 0.4$, and 0.04, respectively) and $\mu_{eff} \approx 7$–$8\mu_B$ due to Eu^{2+} ions, which is in agreement with the theoretical value ($\mu_{eff} \approx 7.94\mu_B$).

From the data of Figs. 1 and 2, we are able to construct the phase diagram for the $Sr_{8-x}Eu_xGa_{16}Ge_{30}$ series, displayed in Fig. 3. The result is in agreement with previous data for $x = 8.0, 6.0, 4.0$.[23]

Guided by the phase diagram, we can start ESR data analysis. Figure 4 shows the *X*-band ESR signal measured at room temperature for $x = 6.0, 2.0, 0.4, 0.04$. Although the

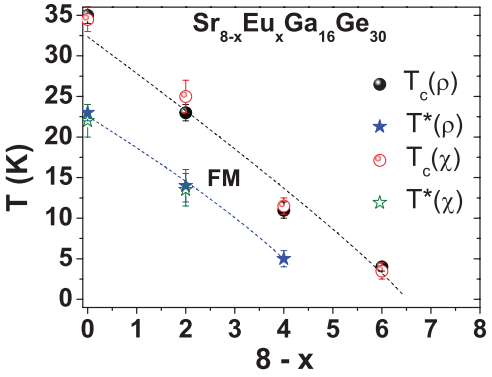

FIG. 3. (Color online) Phase diagram of $Sr_{8-x}Eu_xGa_{16}Ge_{30}$ single crystals.

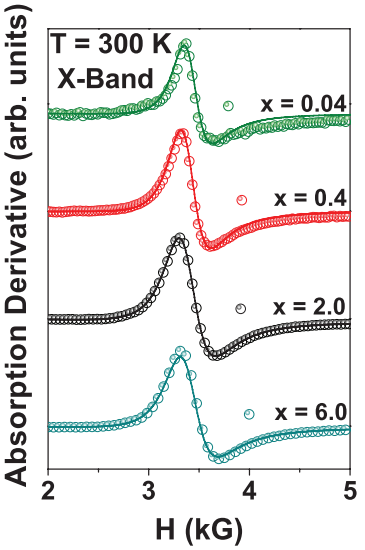

FIG. 4. (Color online) *X*-band ESR lines at $T = 300$ K.

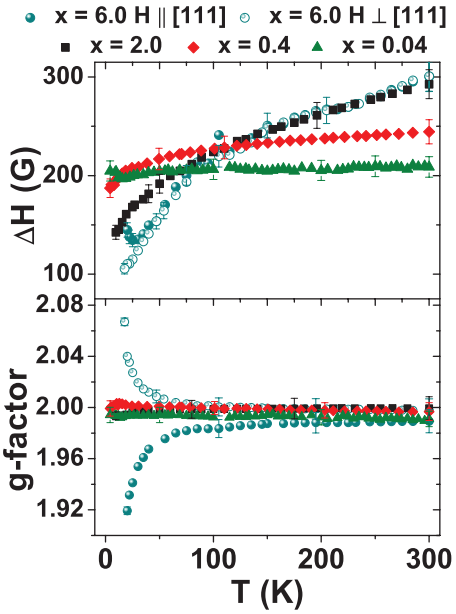

FIG. 5. (Color online) Temperature dependence of the ESR linewidth and g factor for $Sr_{8-x}Eu_xGa_{16}Ge_{30}$ single crystals.

Eu^{2+} ions have two inequivalent sites in the clathrate structure, we observe for all x values a single isotropic Dysonian ESR line with no hyperfine lines, which is characteristic of localized magnetic moments in a lattice with a skin depth smaller than the size of the sample particles.[24] This indicates that these two inequivalent sites are indistinguishable by ESR.

From the fit of the resonances to the appropriate admixture of absorption and dispersion, we obtained for $x \geqslant 2.0$ an isotropic linewidth $\Delta H \approx 310 \pm 20$ Oe in the *X* band, which is in agreement with previously reported values for the pure compound $Eu_8Ga_{16}Ge_{30}$.[20,21] However, in the diluted regime ($x < 2$), there is clearly a narrowing of ΔH, and for the lowest concentration in which we observe ESR resonance ($x = 0.04$), we obtained a T-independent $\Delta H \approx 210 \pm 11$ Oe. This evident narrowing of the ESR linewidth in the Eu-diluted regime is consistent with the decreasing of Eu^{2+}-Eu^{2+} spin-interaction contribution to the ESR ΔH.[25] For all x values, we obtained a g value of $g \simeq 1.998(4)$ at high temperature.

Consider the simplest scenario for the treatment of the exchange interaction, $J_{fs}\mathbf{S}.\mathbf{s}$, between a localized Eu^{2+} $4f$ electron spin ($\mathbf{S}$) and the free ce spins ($\mathbf{s}$) of the host metal, where *bottleneck*, *dynamic*, electron-electron correlation effects, $\mathbf{q}$-dependence exchange, and multiple-band effects are not present.[26] In this simple case, the ESR g shift (Knight shift)[27] and the Korringa rate[28] can be written as

$$\Delta g = J_{fs}\eta(E_F), \tag{1}$$

and

$$\frac{d(\Delta H)}{dT} = \frac{\pi k}{g\mu_B} J_{fs}^2 \eta^2(E_F), \tag{2}$$

where J_{fs} is the effective exchange interaction between the Eu^{2+} local moment and the ce in the absence of ce momentum transfer,[29] $\eta(E_F)$ is the *bare* density of states (DOS) for one spin direction at the Fermi surface (FS), k is the Boltzman constant, μ_B is the Bohr magneton, and g is the $Eu^{2+}g$ value. When Eqs. (1) and (2) are applicable, the relation $\frac{d(\Delta H)}{dT} = \frac{\pi k}{g\mu_B}(\Delta g)^2$ holds. Using the g value of Eu^{2+} in insulators as 1.993(3), $(\pi k/g\mu_B) = 2.34 \times 10^4$ Oe/K, and replacing $\Delta g \approx 0.005(4)$, we found a $b \approx 0.6$ Oe/K for the Eu^{2+} resonance.[30,31] It was proposed in the literature that the relaxation mechanism for the concentrated compound is the Korringa relaxation and the measured Korringa rate is $b \approx 0.8$ Oe/K, which is in agreement with this simple scenario. In fact, Fig. 5 shows that in the concentrated regime ($x \geqslant 2.0$), the high-temperature linewidth behavior is almost the same for all x values, suggesting that the single-band Korringa contribution is dominant.

However, this is in contrast to the suppression of the Korringa rate for the dilute regime ($x < 2.0$). As the obtained g-shift value is constant along the series for all x values, one would expect a constant Korringa rate along the series too. Although the g factors do not change within the error bars of our experiment, it is possible that a small change in the density of states and/or in the Fermi-surface topology is responsible for the change in the Korringa-like component.[32] In fact, the electrical resistivity measurements (see Fig. 1) show that at low temperatures and low Eu concentrations, the resistivity starts to increase slightly, characteristic of semiconducting behavior. Nevertheless, the spin-lattice relaxation via the Eu^{2+}-ce exchange interaction in a single-band picture is not enough to explain the ΔH evolution at low temperatures (see Fig. 5) and higher magnetic fields (see below). In any case, this feature of the Korringa-like component enables us to dismiss *bottleneck* and spin-spin exchange narrowing effects, which would increase the Korringa-like rate with decreasing concentration.[26] The *dynamic* effects can also be dismissed since there is no strong T dependency of the g values. At low-T, we observe a strong anisotropy in the g value as we approach T_c, which is probably due to the anisotropic internal field felt at the Eu^{2+} site.

When the temperature increases and reaches the Einstein temperature (~25–50 K) in the Sr-rich extreme, we do not observe any linewidth narrowing (motional narrowing) as the rattling modes are activated. Therefore, there are no features

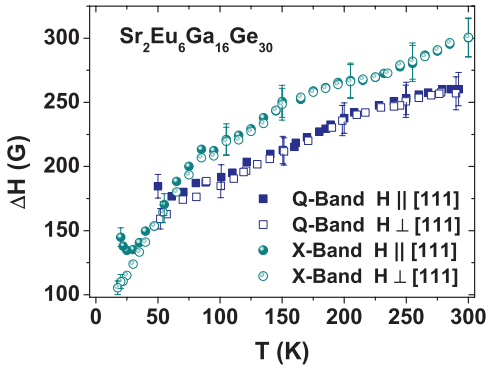

FIG. 6. (Color online) Temperature dependence of the ESR linewidth in X and Q band for $x = 6.0$.

indicating a spin-glass-like behavior even though the Einstein temperature, $\theta_E \approx 60$ K, becomes higher than T_c.[20]

To gain more information about the relaxation mechanism, we performed ESR experiments in the Q band ($\nu \sim 34$ GHz). Figure 6 displays the temperature dependence of the linewidth in both X and Q bands for $x = 6.0$. We choose this concentration since it is the one that shows the more dramatic narrowing as a function of temperature. Surprisingly, there is a line narrowing at higher fields, indicating that the resonance is homogeneous in the paramagnetic phase. In order to understand this behavior, different contributions to the ESR linewidth must be considered. There are two types of resonant line broadening in solids: homogeneous and inhomogeneous broadening. Homogeneous ESR linewidth is inversely proportional to the *spin-spin* relaxation time, T_2.[30] It occurs when the magnetic-resonance signal results from a transition between two levels of spins which are not sharply defined, but instead are somewhat intrinsically broadened. The main contributions to homogeneous broadening are (1) dipolar interaction between like spins, (2) spin-lattice interaction, (3) interaction with radiation field, (4) diffusion of excitation throughout the sample, and (5) motionally narrowing fluctuations of local fields.[30,33]

On the other hand, an inhomogeneously broadened resonant line is one which consists of a spectral distribution of individual lines merged into an overall line or envelope. For instance, a distribution of local fields caused by unresolved fine and/or hyperfine structure, g-value anisotropy, strain distribution, and/or crystal irregularities that exceed the natural linewidth ($2/\gamma T_2$, γ is the gyromagnetic factor) will cause the spins in various parts of the sample to feel different field strengths.[30,33]

In this way, the resonance will be artificially broadened in an inhomogeneous manner. In the cases of inhomogeneous broadening caused by g-value anisotropy and related strain distribution and/or crystal irregularities, the ESR linewidth is expected to increase as a function of magnetic field. From the linewidth ΔH data in Fig. 6, we can conclude that the isotropic ESR ΔH revealed a homogeneous contribution, as it presents a measurable narrowing at the Q band, and thus there is no distribution of g values. Moreover, above $T = 100$ K at X and Q bands and at any Eu^{2+} concentration, the spectra do not show angular dependence, and thus they are isotropic with no unresolved fine structure. Besides these two arguments, at 300 K, the X-band linewidth narrows as the concentration of Eu decreases, making clear that there is no exchange narrowing effects and that the inhomogeneous broadening due to the unresolved fine structure is not relevant to our analysis. One necessary condition for the observance of exchange narrowing effects is that the homogenous linewidth of the ESR transition has to be essentially smaller than the exchange narrowed linewidth.

Second, for strong exchange narrowed systems, due to the coupling between the resonating spins and the conduction electrons, at low temperatures the ESR line starts to broaden and the collapsed fine-structure lines would become resolved. In this case, exchange narrowing is important to analyze the T dependence of the ESR linewidth. This behavior was also not observed in our experiments. Thus, the ESR linewidth is dominated by the homogeneous linewidth. As in the case of EuB_6,[22] these features of the homogeneous ESR linewidth can only be explained by magnetic polaronic effects.

There are few mechanisms that can trigger the linewidth narrowing at higher magnetic fields, e.g., dipolar interactions, magnetostriction, and magnetic polarons. Dipolar interactions are short-range interactions that depend on the distance between magnetic neighbors. Since this distance is not expected to change drastically with temperature and magnetic field, one would expect a weak H and T dependence of the linewidth. In fact, the dipolar interaction cannot explain the strong ΔH T dependence. Moreover, there is no evidence for magnetostriction in this class of materials.[4,5,10] Therefore, these two phenomena cannot be the source of narrowing. In this manner, the experimental data strongly suggest that the main contribution to the relaxation comes from the formation of magnetic polarons. In this scenario, the spin of the conduction electron polarizes the Eu^{2+} spins in its neighborhood, thus creating a ferromagnetic spin cloud that follows the ce when it moves through the crystal. Therefore, the low-T reduction of the linewidth is a consequence of the decrease in the spin-flip scattering rate [which occurs via the exchange interaction, J_{fs} **S.s**, between a localized Eu^{2+} $4f$ electron spin (**S**) and the free conduction electron spins (**s**)] as the magnetic polarons grow. Eventually, the polarization clouds percolate at T_c and long-range ferromagnetic correlations are established. At high T, the reduction of the spin-flip scattering when H increases leads to a reduction in the linewidth and to a negative magnetoresistance due to the formation of larger magnetic polarons. Obviously, as we decrease the Eu content, we also decrease the formation of magnetic polarons. This explains the much smaller linewidth decrease at low T and the smaller ΔH reduction at higher fields for the diluted compounds.

IV. CONCLUSION

In summary, single crystals of $Sr_{8-x}Eu_xGa_{16}Ge_{30}$ were characterized by electrical resistivity, magnetic susceptibility, and electron spin-resonance experiments. Both magnetic transitions were mapped as a function of x and the phase diagram was obtained. From the Eu^{2+} ESR analysis on the single Dysonian line, we have found strong evidence for the formation of magnetic polarons. Strikingly, as T is lowered and H is increased, there is a decrease in the conduction electron spin-flip scattering. On the other hand, no evidence for a spin-glass behavior was found in this material, suggesting

that the coupling between the rattling modes and the electronic degrees of freedom is weak. Moreover, the rattling Einstein temperature of $\theta_E \approx 25$–60 K leads to a rattling frequency of approximately 800 GHz, which is much higher than the *X*-band microwave frequency (9 GHz).

ACKNOWLEDGMENTS

We would like to acknowledge support by the Brazilian agencies FAPESP (in particular, Grants No. 2006/60440-0, No. 2009/09247-3, No. 2010/11949-3, No. 2011/01564-0, and No. 2011/23650-5), CNPq, and CAPES.

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