Transition from a mixed-valent system to a magnetically ordered Kondo lattice in $Ce(NiSi)_{2-x}(CuGe)_x$

G. Liang and Robert Barber
Department of Physics, Sam Houston State University, Huntsville, Texas 77341

Yijie Tang
Department of Chemistry, Sam Houston State University, Huntsville, Texas 77341

M. Croft
Department of Physics, Rutgers University, Piscataway, New Jersey 08855

J. L. Cobb and J. T. Markert
Department of Physics, University of Texas at Austin, Austin, Texas 78712
(Received 31 May 1994)

The crossover from mixed-valent to magnetically ordered Kondo or heavy-fermion behavior in $Ce(NiSi)_{2-x}(CuGe)_x$ has been studied. Results of Ce L_3-edge, structural, magnetic, and transport measurements are presented. It is suggested that the abnormal increase of the lattice parameter c in the region $1.6 \leq x \leq 2.0$ be irrelevant to the Ce $4f$-ligand orbital dehybridizations and the associated heavy-fermion state. Our results show that the substitution for Cu (and Ge) for Ni (and Si) drives this series from a strong mixed-valent to an antiferromagnetically ordered trivalent Kondo-lattice system. Particularly, it is found that the physical properties of the $x=1.4$ compound are very similar to that of the heavy-fermion superconductor $CeCu_2Si_2$. The resistivity data also indicate that there is an active interplay between the crystalline electric field, coherence effects, and Kondo scattering. Moreover, this study supports the proposal that the Kondo-type spin fluctuation can be effectively quenched by the internal $3d$-host magnetic field in some $CeMn_2Si_2$-based materials. Magnetic susceptibility data show that this compound series is antiferromagnetically ordered for $x > 1.6$ and the spin-fluctuation temperature T_{sf} decreases with increasing x in this region. A phase diagram is proposed to illustrate the evolution of the series from a single-impurity Kondo to a coherent Kondo and then to an antiferromagnetically ordered system.

I. INTRODUCTION

The 1:2:2-type intermetallic compounds CeM_2X_2 with M = transition metal and X = Si or Ge, have been the subject of ongoing interest for studies of unique and diverse mixed-valence (MV), Kondo effect, and heavy-fermion (HF) behavior.[1-3] For example, $CeCu_2Si_2$ is a Kondo-lattice/heavy-fermion superconductor with very weak valence mixing,[3,4] while $CeMn_2Si_2$ is a mixed-valent system which also exhibits a strong $3d$-host magnetism.[5] However, heretofore, no studies have been carried out for a single Ce 1:2:2 series in which the Ce valence spans the entire valence range of the Ce 1:2:2 materials. A study of such series is very valuable for understanding the entire evolution of a system from a high valence state to a trivalent state (which may or may not be a Kondo-HF state). The $Ce(NiSi)_{2-x}(CuGe)_x$ series is ideal for such study because the $x=0$ compound $CeNi_2Si_2$ is a strongly mixed-valent system with a spin-fluctuation temperature T_{sf} as high as 600 K (Ref. 6) and a Ce L_3 valence (v_3) as high as 3.17 (nearly the highest value for all of the Ce 1:2:2 compounds) and the $x=2$ compound $CeCu_2Ge_2$ is a trivalent system with $v_3=3.0$.[7]

There are a number of additional motivations for studying the $Ce(NiSi)_{2-x}(CuGe)_x$ series as noted below. First we hope to clarify whether the dehybridization of ligand orbitals with Ce is indeed essential for forming the heavy-fermion ground state in $CeCu_2Si_2$. This conjecture was proposed by Sampathkumaran and Vijayaraghavan[6] based on the observed anomalous increase of the c parameter near the $x=2$ end of the $CeNi_{2-x}Cu_xSi_2$ series. Since the reported γ value for $CeCu_2Ge_2$ is only about 0.11–0.13 J/K^2 mol as $T \to 0$ (almost an order of magnitude smaller than the γ of $CeCu_2Si_2$),[3,8] the study of the c parameter of the $Ce(NiSi)_{2-x}(CuGe)_x$ series provides an opportunity to test the role of such dehybridization in the formation of the HF ground state. Second, it has been reported that $CeCu_2Ge_2$ is a Kondo-lattice system with antiferromagnetic ordering occurring at $T_N=4.15$ K.[8-10] It is therefore possible that for certain x values (say near $x=1.4$) the $Ce(NiSi)_{2-x}(CuGe)_x$ system could becomes a heavy-fermion superconducting system similar to $CeCu_2Si_2$. This is expected because the double substitution of Ge (and Cu) for Si (and Ni) should speed up the MV→Kondo/HF process when compared with the single-element substitution in the $CeNi_{2-x}Cu_xSi_2$ series. Thus, studying the $Ce(NiSi)_{2-x}(CuGe)_x$ series in the entire x range could provide us with information regarding

the necessary conditions (such as Ce valence and T_{sf}) for forming the HF ground state. In addition, studying this system will also provide information about the competition between the Kondo-type spin-fluctuation (Kondo scattering) and the Ruderman-Kittel-Kasuya-Yosida (RKKY) magnetic interaction[9,11] near the $x=2$ end of the series.

Another motivation to study this series is to further clarify the interesting $3d$-$4f$ interaction in some recently studied magnetic $3d$-host Ce compounds.[12,13] A recent study of the MV-Kondo system $CeMn_2Si_{2-z}Ge_z$ showed that the Ge for Si substitution induces remarkable crystalline electric-field (CEF) modified Kondo-lattice behavior and it appeared that the relatively lower-energy-scale Kondo-type spin fluctuations were basically quenched by a higher-energy-scale $3d$ internal magnetic field generated by the ferromagnetically ordered Mn sublattice.[13] It is not completely clear whether this Kondo quenching is predominantly due to the $3d$-$4f$ interaction or just the crystal expansion (caused by the substitution of smaller element Si by the larger element Ge). In this compound series, the Ce L_3 valence v_3 spans a range from a moderate MV to complete trivalent ($3.12 \geq v_3 \geq 3.00$). Clarifying the correlation between such strong $3d$-host field and Kondo scattering is important, because it could demand a proper modification of the Anderson Model[14] to incorporate the right form of Ce $4f$-Mn $3d$ magnetic interaction for further studying these magnetic $3d$-host materials. The best such clarification is to compare this magnetic $3d$-host series with a nonmagnetic $3d$ series which spans a similar (or wider) Ce-valence range and exhibits also Kondo-lattice behavior. It appears that the $Ce(NiSi)_{2-x}(CuGe)_x$ series is the best choice for this purpose because $CeCu_2Ge_2$ is a trivalent Kondo lattice and the series has the same $ThCr_2Si_2$ structure with a structure Ge for Si substitution. In this paper we report the lattice parameter, Ce L_3-edge, magnetic susceptibility, and resistivity results.

II. EXPERIMENTAL

The samples used in this study were polycrystalline samples prepared by arc melting stoichiometric amounts of the constituent elements in an argon atmosphere. X-ray-diffraction measurements were made using an automated SCINTAG-PAD-V powder diffractometer and all samples were confirmed to be single phase with the $ThCr_2Si_2$ structure. The lattice parameters were obtained by the least-squares fitting of the x-ray-diffraction patterns in the range of $20° \leq 2\theta \leq 80°$. The resistivity $\rho(T)$ measurements were made by a standard four-probe dc technique in a temperature range of 1.7–300 K. The magnetic-susceptibility measurements, $\chi(T)$, were performed using a superconducting quantum interference device magnetometer. The Ce L_3-edge spectra were taken at National Synchrotron Light Source and Ce L_3-valence determination method has been described elsewhere.[7,15]

III. RESULTS AND DISCUSSION

A. L_3-edge and lattice-parameter results

L_3-edge x-ray-absorption spectroscopy (XAS) has been proven to be a very valuable technique for measuring the valence of elements in a compound.[13,15,16] In Fig. 1 we show the Ce L_3-edge spectra for $Ce(NiSi)_{2-x}(CuGe)_x$ samples, with all spectra normalized to the low-energy (Ce^{3+}) peak. A higher-energy (Ce^{4+}) peak, at about 9 eV above the lower-energy peak, is quite prominent for the $x=0$ sample $CeNi_2Si_2$. This Ce^{4+} feature gradually weakens with increasing x and finally disappears for $x>1.2$. This indicates that Ce in this system has become nearly trivalent at $x=1.2$. The Ce L_3 valence v_3, determined by our curve fitting method,[7,15] is plotted versus x in Fig. 2 (bottom). The v_3 value for the $x=0$ sample is 3.17, indicating that $CeNi_2Si_2$ is a strongly mixed-valent compound. With increasing x, v_3 decreases rapidly from 3.17 at $x=0$ to 3.07 at $x=0.6$, and slowly beyond $x=0.6$ reaching finally 3.0 at $x=2$ for $CeCu_2Ge_2$. The $v_3(x)$ curve exhibits a nonlinear behavior, as observed in a number of other Ce systems such as $CeMn_2Si_{2-z}Ge_z$.[13]

In a previous work[17] we have proposed a MV-Kondo regime borderline nominally in the range $3.07 \leq v_3 \leq 3.10$ (at room temperature) for CeT_2Si_2 systems with T being the $3d$ transition metals. Here the lower end of the v_3 borderline occurs near $x=0.6$ for the $Ce(NiSi)_{2-x}(CuGe)_x$ samples, below which v_3 manifests a stronger x variation. Such a MV to Kondo regime crossover near $x=0.6$ is further supported by our resistivity results discussed below.

The lattice parameters, a and c, are reported also in Fig. 2 as functions of x. It can be seen both a and c deviate from Vegard's law with different signs. The $a(x)$ curve of the $Ce(NiSi)_{2-x}(CuGs)_x$ is very similar to that of the $CeNi_{2-x}Cu_xSi_2$ and $CeMn_2Si_{2-z}Ge_z$ series, i.e., a rapid increase of a below $x=1.2$ followed by a slower increase as x approaches 2.0.[6,13,18] The c versus x curve

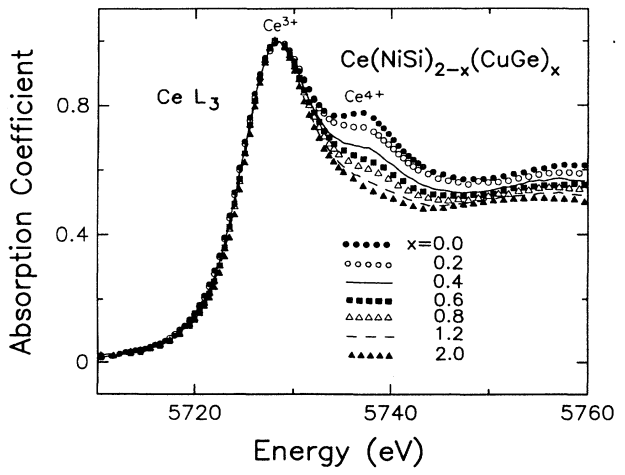

FIG. 1. The Ce L_3 absorption spectra of $Ce(NiSi)_{2-x}(CuGe)_x$ samples, all normalized to the Ce^{3+} peak.

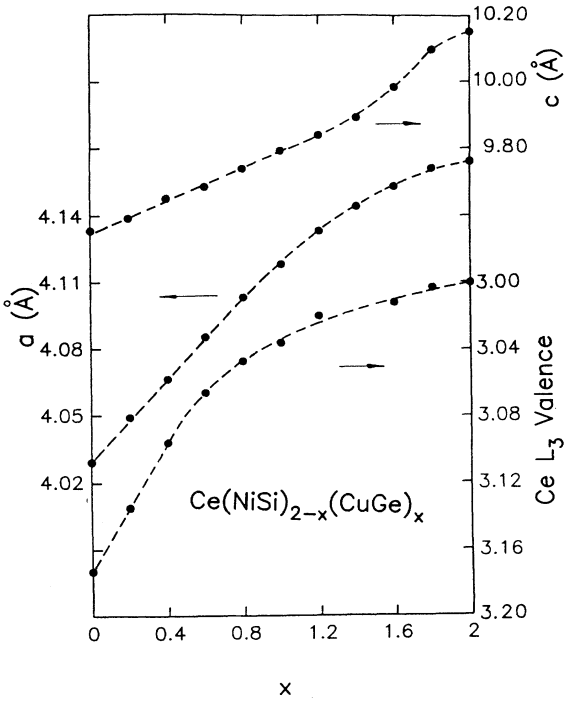

FIG. 2. The lattice parameters a and c, and the Ce L_3 valence (v_3) of the Ce(NiSi)$_{2-x}$(CuGe)$_x$ system. The dashed lines are guides to the eye.

manifests a very similar behavior to the $c(x)$ curve of $CeNi_{2-x}Cu_xSi_2$ in the whole range of x. They both have an almost linear change with x in the $0 \leq x \leq 1.4$ region and present an anomalous bump in the region of $x \geq 1.6$. Thus, compared with the $CeNi_{2-x}Cu_xSi_2$ system, it seems that the consequence of the additional Ge for Si substitution in the Ce(NiSi)$_{2-x}$(CuGe)$_x$ alone is only a linear variation of the c parameter with x, as observed previously in the whole z range (i.e., $0.0 \leq z \leq 2.0$) of the magnetic 3d-host $CeMn_2Si_{2-z}Ge_z$ series.

The increase in c parameters as x varies from 1.6 to 2.0 in the $CeNi_{2-x}Cu_xSi_2$ has been cited by Sampathkumaran and Vijayaraghavan[6] as an evidence for a dehybridization of the Ce 4f orbital from the (Ni,Cu)-Si ligand orbitals. Moreover, Sampathkumaran and Vijayaraghavan[6] proposed that this dehybridization process was an integral to the formation of the HF state in the $x=2$ endpoint compound $CeCu_2Si_2$. We note that the lattice parameter variations in our Ce(NiSi)$_{2-x}$(CuGe)$_x$ system are qualitatively similar to those in the $CeNi_{2-x}Cu_xSi_2$ system. In particular the nonlinear c-axis expansion approaching $CeCu_2Ge_2$ is similar to that emphasized by Sampathkumaran and Vijayaraghavan[6] in the approach to $CeCu_2Si_2$. de Boer *et al.* have, however, clearly shown that the electronic specific-heat coefficient γ for $CeCu_2Ge_2$ is merely 0.11–0.13 J/K^2 mol (roughly an order of magnitude smaller than in $CeCu_2Si_2$ and out of the HF range). Thus, this c-parameter anomaly would appear to be essentially independent of the HF character of these two endpoint compounds.

The above observation contradicts the existence of a dehybridization-HF coupling. In this regard it is enlightening to note the work of Liang *et al.*[18] on the $LaNi_{2-x}Cu_xSi_2$ system, which clearly demonstrated parabolic deviations (negative for the c parameter and positive for the a parameter) in the $LaNi_{2-x}Cu_xSi_2$ system. In this system the La-4f^0 character removes the Ce-4f^1-hybridization issue and the well-known parabolic-type Vegard's-law deviation produces a similar upturn in the c parameter approaching the endpoint compound. The evidence at hand suggests that parabolic Vegard's-law deviations are the rule in these systems and moreover that Ce-related contributions to the lattice parameters must be superimposed on this background. Since the observations of Sampathkumaran[6] and Vijayaraghavan[6] were explicitly based on the Vegard's-law assumption, one is forced to conclude that there is, as of now, no real structural evidence for a "dehybridization effect" in any of these materials. Possibly, there may be some deviation from a simple parabolic c-parameter variation in the $x \geq 1.8$ region of the Ce compounds, however much more detailed studies are required before the existence and origin of such an effect can be clarified.

B. Magnetic susceptibility

Shown in Fig. 3 is the inverse magnetic susceptibility $\chi^{-1}(T)$ data for the $x=1.8$ and 2.0 samples. The $\chi^{-1}(T)$ curve for the $x=1.6$ sample is omitted in Fig. 3 because it is very close to that of the $x=1.8$ sample. The data shows typical crystalline electric-field (CEF) modified rare-earth free ion behavior:[19] a crossover curvature between a high-T Curie-Weiss region (here 100 K $\leq T \leq$ 300 K) and a low-T Curie-Weiss region (here from about 15 K down to the Néel temperature). The data in these two temperature ranges can be well fitted to $\chi = C/(T+\Theta)$, where $C = N\mu_{\rm eff}^2/3k_B$, $\mu_{\rm eff}$ is the effective moment, and Θ is the Curie-Weiss temperature. The high-T $\mu_{\rm eff}$ values for $x=1.6$, 1.8, 2.0 samples are $2.64\mu_B$, $2.60\mu_B$, and $2.51\mu_B$, respectively, and the corresponding Θ values are 54.4, 45.7, and 25.7 K. These $\mu_{\rm eff}$ values are quite close to the free-ion Ce^{3+} value $2.54\mu_B$/Ce (in its $^2F_{5/2}$ Hund's rule ground state) and are consistent with our Ce L_3 valence conclusion results that these three samples are very close to being trivalent. Note that $\mu_{\rm eff}$ value ($2.51\mu_B$) measured here for $CeCu_2Ge_2$ is in sharp contrast with the value $\mu_{\rm eff}=2.1\mu_B$ previously reported by de Boer *et al.*[8] The low-T effective moment values for the $x=1.6$, 1.8, and 2.0 samples are $1.94\mu_B$, $1.83\mu_B$, and $2.11\mu_B$, respectively. This reduction of $\mu_{\rm eff}$ can be well explained by the CEF doublet ground-state schemes proposed for Ce^{3+} in $CeCu_2Si_2$.[20,21] Qualitatively, if the CEF level scheme in our system is assumed to be similar to that in $CeCu_2Si_2$,[20,21] then the dominant population of the Ce^{3+} ions would be in the doublet CEF ground state at low temperature. Lieke *et al.*[4] used the wave functions of the CEF ground state doublet, Σ_7^t, to calculate the $\mu_{\rm eff}$ value of $CeCu_2Si_2$ and obtained a value of $\mu_{\rm eff}(T \to 0) \approx 1.65\mu_B$/Ce. The slightly larger value of the measured

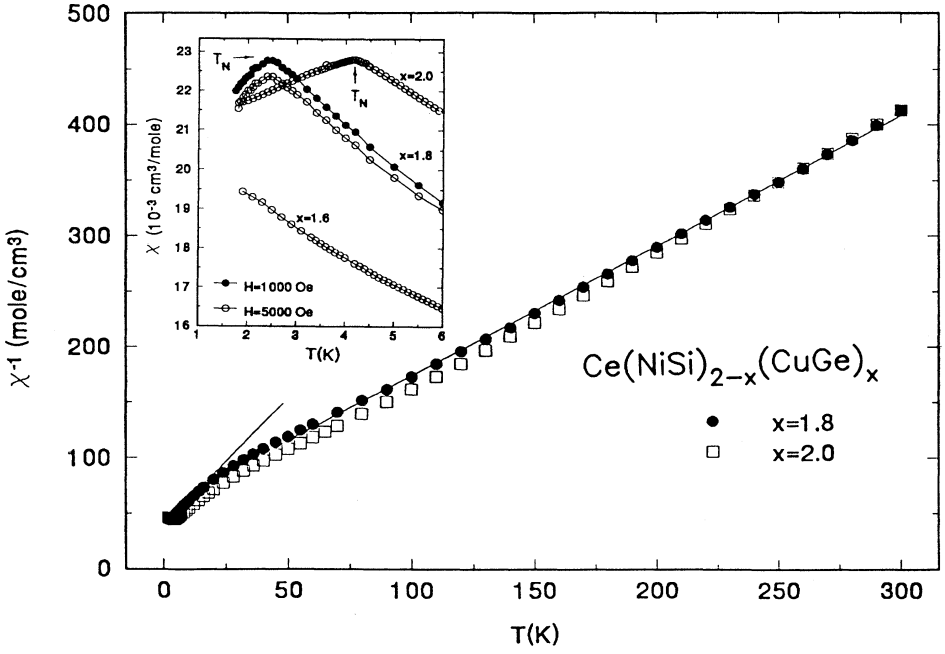

FIG. 3. Temperature dependence of the inverse magnetic susceptibility $\chi^{-1}(T)$ of the sample $Ce(NiSi)_{2-x}(CuGe)_x$ with $x=1.8$ and 2.0, measured in a field of 5000 Oe. The two straight solid lines through the $\chi^{-1}(T)$ data points are the fit $\chi^{-1}=(T+\Theta)/C$ to the data points in a high-T region 100 K $\leq T \leq 300$ K and a low-T region 4.2 K $\leq T \leq 15$ K. Inset shows the low-temperature $\chi(T)$ data for three samples with $x=1.6$, 1.8, and 2.0.

μ_{eff} (compared with the calculated one) may indicate a small fractional population of the excited CEF states at these temperatures.

The inset of Fig. 3 presents the $\chi(T)$ curves of these three samples at low temperature. The $x=2.0$ and 1.8 samples were found to be antiferromagnetic (AF) ordered at the Néel temperatures (T_N), which can be defined as the cusp temperature obtained by extrapolating the high- and low-T side of the cusp of the $\chi(T)$ curves. The T_N value for $x=2$ sample $CeCu_2Ge_2$ is 4.15 K, the same as the value previously reported.[8] For the $x=1.8$ sample, we found that $T_N=2.47\pm0.05$ K from the 1000-Oe data and $T_N=2.41\pm0.05$ K from the 5000-Oe data. The shift in T_N to lower temperatures with increasing field is consistent with antiferromagnetic ordering. Obviously, T_N for the $x=1.8$ sample is depressed relative to the $x=2$ sample $CeCu_2Ge_2$. No magnetic ordering was found down to 1.9 K for the $x=1.6$ sample, indicating that the borderline between nonmagnetic and magnetic phases in the present series is between $x=1.6$ and 1.8. Correlating with the x dependence of the lattice parameters and Ce valence (see Fig. 2), we see that T_N in this series decreases with decreasing lattice parameter (i.e., increasing internal pressure) or increasing Ce valence. Similar depression of T_N has also been found by applying external pressure to $CeCu_2Ge_2$.[10]

It is worthwhile to discuss the x dependence of $\chi^{(0)}$ because it is believed that for MV-Kondo systems, $C/2\chi(0)$ (where C is the Curie constant for free ions) is equal to the spin-fluctuation temperature,[6,22] T_{sf}, and $\chi(0)$ is itself directly related to the linear specific-heat coefficient γ.[2,22] A general rule is that both T_{sf} and $\chi^{-1}(0)$ decrease continuously when a Ce compound series varies from a MV to a trivalent system (which usually is accompanied by an increase in lattice parameters). Indeed, this behavior has been observed in the MV-Kondo-lattice system $CeNi_{2-x}Cu_xSi_2$ inspite of the presence of the strong CEF (which sometimes could markedly affect the low-temperature $\chi(T)$ values for trivalent materials[2]). Due to the AF ordering at temperatures below 4.15 K, we will use the $\chi(4.2\text{ K})$ values to approximate the $\chi(0)$. The measured $\chi(4.2\text{ K})$ values for $x=1.6$ 1.8, and 2.0 samples are 0.017, 0.021, and 0.023 cm^3/mol, respectively. This increase of $\chi(4.2\text{ K})$ with increasing x when correlated with the x dependence of the lattice parameters and L_3-XAS results in Fig. 2, is in agreement with the general rule mentioned above.

Compared with the smaller $\chi(4.2\text{ K})$ (~ 0.013 cm^3/mol)[6] and larger v_3 (~ 3.05) values of the HF system $CeCu_2Si_2$, we see that the three samples (with $1.6\leq x\leq 2.0$) studied here are closer to trivalent and they should have smaller T_{sf} than that of $CeCu_2Si_2$. Indeed, the measured $C/2\chi(0)$ ($=T_{\text{sf}}$) values in this series support this conclusion. The formula $T_{\text{sf}}=C/2\chi(0)$ has been used for estimating T_{sf} of a number of trivalent Kondo-lattice systems such as $CeRu_{2-y}Os_ySi_2$ series.[22] For the present series, since the μ_{eff} values obtained from the high-T ($100\leq T\leq 300$ K) $\chi(T)=C/(T+\Theta)$ fitting are close to that of the Ce free-ion value, we can use the C values obtained from this high-T fitting for estimating $C/2\chi(0)$. The C values obtained from the high-T fitting are 0.78, 0.84, 0.87 $\text{cm}^3\,\text{K/mol}$ for the $x=2.0$, 1.8, and 1.6 samples, respectively. The C value estimated from the $\chi^{-1}(T)$ data of Ref. 19 is 0.90 cm K/mol for $CeCu_2Si_2$. If we assume that the ratio $R=\chi(4.2\text{ K})/\chi(0)$ (in the absence of the magnetic ordering) is the same for these four compounds and use the value $T_{\text{sf}}=10$ K (see Ref. 24) for $CeCu_2Si_2$, then the T_{sf} values, estimated by using the formula $T_{\text{sf}}=RC/2\chi(4.2\text{ K})$, are about 4.9, 5.8, and 7.4 K for the $x=2.0$, 1.8, and 1.6 samples, respec-

tively. One should note that since the T_N (=4.15 K) for the $x=2.0$ compound is very close to 4.2 K, there should be a substantial decrease of the χ (4.2 K) for this sample due to long-range magnetic interactions. Thus the T_{sf} value estimated above from the $x=2.0$ sample is overestimated, i.e., the actual T_{sf} for this compound should be much smaller than 4.9 K. By the same reason, the T_{sf} value should have been slightly overestimated for the $x=1.8$ sample but not overestimated for the $x=1.6$ sample.

C. Resistivity results

1. Temperature dependence of resistivity

In Figs. 4 and 5 we present the $\rho(T)$ results for the entire $Ce(NiSi)_{2-x}(CuGe)_x$ series. The $\rho(T)$ results (1.7 K $\leq T \leq 300$ K) are qualitatively similar to that observed in $CeNi_{2-x}Cu_xSi_2$ series, but with a relatively faster passage from the MV to Kondo regime due to the additional Ge for Si substitution. The resistivity involves not only the interplay of the MV/Kondo, CEF, and narrow-band coherent effects but also the magnetic ordering of the Ce sublattice. The $\rho(T)$ data can be discussed in the following three regions for the series:

$0.0 \leq x < 0.6$: This region is a MV regime with Ce L_3 valence v_3 between 3.17 and 3.07. The $\rho(T)$ data in Fig. 4 shows a positive temperature coefficient of resistivity (TCR) at all temperatures. This type of phonon-scattering-dominated behavior is very typical for high Ce-valence materials in which the Kondo scattering from the Ce-4f spins is essentially quenched. A $\rho(T)=\rho_0+bT^2$ (with ρ_0 and b constants) behavior was found for $0<x\leq 0.6$ but not for the $x=0$ samples: in the temperature range 2 K $\leq T \leq 90$ K for $x=0.2$ and 0.4 samples and 2 K $\leq T \leq 20$ K for $x=0.6$ samples. This temperature dependence of $\rho(T)$ is quite similar to the high-pressure (112 kbar $\leq p \leq 197$ kbar) resistivity results reported by Bellarbi *et al.* and DiMarzio, Liang, and Croft[23] for $CeCu_2Si_2$. The $\rho(T)$ curve and Ce L_3-valence values in this region are very close to the MV region $0.0 \leq x \leq 1.0$ for the $CeNi_{2-x}Cu_uSi_2$ series.[18]

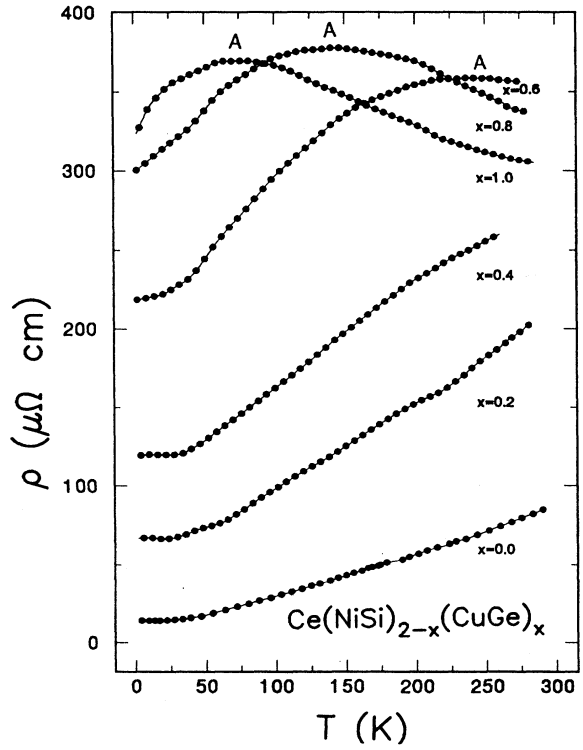

FIG. 4. The electric resistivity vs temperature for the $Ce(NiSi)_{2-x}(CuGe)_x$ systems with $0.0 \leq x \leq 1.0$. The letter A is used to indicate the position of the broad resistivity maximum, which moves towards lower temperature with increasing x.

$0.6 \leq x \leq 1.0$: In this range of x, the Ce L_3-valence v_3 ranges from 3.07 to 3.04 which places the samples in the Kondo local-moment regime.[17] We see in Fig. 4 an appearance of a broad structure in the $\rho(T)$ curves with a resistivity maximum labeled by the letter A. With increasing x, the region where a negative TCR (due to single-impurity Kondo scattering) is observed is pushed to lower temperature. The variations in the temperature of the resistivity maximum A, T_A, have been used in MV-Kondo/heavy-fermion systems in the past to qualitatively estimate the variation of T_{sf} (or Kondo temperate T_K). T_A is expected to track T_{sf}.[24,25] The observed T_A values are 241, 139, and 73 K for the $x=0.6$, 0.8, and 1.0 samples, respectively. This indicates that T_{sf} moves steadily towards lower temperature with increasing x or decreasing Ce valence (see Fig. 2), in agreement with the single-impurity Kondo scattering theory.[24] The absence of the CEF double-peak feature in the $\rho(T)$ curves indicates that in these three samples $k_BT_K > \Delta_{CEF}$.

$1.0 < x \leq 2.0$: The system in this x range belongs to nearly trivalent/trivalent Kondo regime where the Ce L_3 valence is between 3.04 and 3.00. The $\rho(T)$ curves shown in Fig. 5 exhibit typical CEF modified Kondo-lattice behavior,[24–26] i.e., a double-peak feature (labeled by letters A and C) with a low-temperature coherence drop below T_A. The double-peak $\rho(T)$ can be well interpreted in terms of CEF modified single-impurity Kondo scattering as treated by Cornut and Coqblin,[27] with the CEF scheme (in which the approximate CEF splitting between the doublet ground state and the first excited doublet state $\Delta_{CEF} \sim 140$ K) proposed by Horn *et al.*[20] The double-peak feature starts to grow at $x=1.2$, indicating that in this sample $k_BT_K \sim \Delta_{CEF}$. The following effects are observed in Fig. 5. (1) T_A decreases with the increase of x from $x=1.2$ to $x=1.6$ ($T_A=19.0$, 8.6, and 5.0 K for $x=1.2$, 1.4, and 1.6 samples, respectively) and then is almost unchanged for $1.6 \leq x \leq 2.0$. (2) The temperature (T_B) of the $\rho(T)$ minimum B also drops steadily with increasing x; the T_B values are about 45, 37, 22 K for $x=1.6$, 1.8, and 2.0 samples, respectively (this is consistent with the decrease of T_K). (3) The amplitude ratio of the peak A to the broad feature C decreases with increasing x, consistent with the decrease of T_B, i.e., the observation (2). (4) The position of the broad C feature is observed to be insensitive to the variation of x, indicating that the CEF splitting Δ_{CEF} varies little in this series.

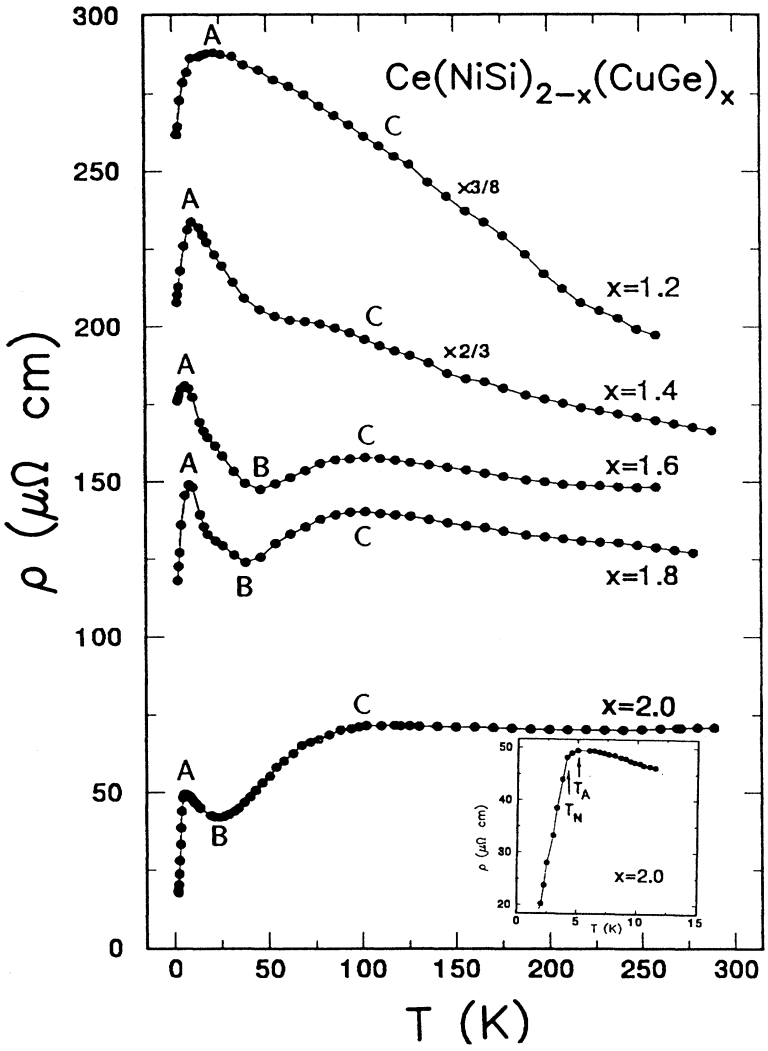

FIG. 5. The electric resistivity vs temperature for the $Ce(NiSi)_{2-x}(CuGe)_x$ system with $1.0 < x \leq 2.0$. The meaning of features *A*-*C* has been described in the text. Inset shows the two-step drop of the low-T resistivity of $x = 2$ sample, which is caused by the coherence effect and AF ordering of the Ce-4*f* sublattice.

Observations (1) through (3) indicate that the (CuGe) for (NiSi) substitution shifts the T_K (or T^* in the case of a Kondo lattice)[10,25] towards lower temperature. It is useful to compare our results with those on a similar series, $Ce_yLa_{1-y}Cu_2Si_2$ with $0.4 \leq y \leq 1.0$.[24] The $\rho(T)$ curves for $y \leq 0.7$ in that study are quite similar to those with $x \leq 1.6$ of the present study with the T_A matching well with T_K (or T_{sf}) within 2 K.[24] Thus, the T_K (or T_{sf}) values for $x \geq 1.6$ samples of the present series, estimated from the T_A values, should be in the range of $T_K \leq 8$ K. This is in full agreement with the T_{sf} values estimated using the magnetic-susceptibility data above.

We observed that the $\rho(T)$ curves of the $x = 1.8$ and 2.0 samples display a precipitous drop below the peak *A* (see the inset of Fig. 5 and also Fig. 7). This kind of drop can be attributed to the setting in of the magnetic ordering in these two samples. The closeness of T_N and T_K indicates that the Kondo scattering energy and the RKKY magnetic interaction energy[11] are competitive in the $x > 1.6$ region, as discussed by Steglich *et al.*[9] for $CeCu_2Ge_2$. The crossover from $T_N > T_K$ to $T_N < T_K$ occurs at $x \sim 1.8$, below which the compression of the lattice parameter (and so the increase of the exchange parameter J) with increasing x increases T_K rapidly, and the Kondo scattering dominates the RKKY magnetic ordering process, as predicted in Doniach's approach.[11]

The $\rho(T)$ curves of the $1.2 \leq x \leq 2.0$ samples of the present series stand in sharp contrast with those of the $CeMn_2Si_{2-x}Ge_z$ series in the same concentration range (i.e., also in $1.2 \leq z \leq 2.0$) where the $\rho(T)$ curves are all dominated by a photonlike positive slope. The Ce L_3 valence in this x or z range, i.e., $3.0 \leq v_3 \leq 3.02$, is the same for both series. Thus, our results here support the proposition[13] that the internal 3*d*-host magnetic field generated by the ferromagnetically ordered Mn sublattice plays a role in quenching the Kondo scattering in the $CeMn_2Si_{2-x}Ge_z$ series, which otherwise would be as thriving as in the present nonmagnetic 3*d*-host series.

It is interesting to note that the $\rho(T)$ curve of the $x = 1.4$ sample is very similar to that of the Kondo-lattice/heavy-fermion system $CeCu_2Si_2$. This indicates that (CuGe) for (NiSi) substitution, at a level of $x = 1.4$, has already driven this series into a regime in which the T_{sf}, Kondo scattering strength, local Ce-4*f* environment,

and CEF scheme are all close to those of $CeCu_2Si_2$. Indeed, a linear extrapolation of the T_{sf} vs x data for the $x=1.6$ and 1.8 samples (see the end of Sec. III B) yields a value of $T_{sf}\approx 10$ K for $x=1.4$, which is exactly the same as that for $CeCu_2Si_2$.[24] This conclusion is also strongly supported by the closeness of the values of T_A, the Ce L_3 valence v_3, and the lattice parameters a and c of $Ce(NiSi)_{0.6}(CuGe)_{1.4}$ and $CeCu_2Si_2$. Specifically, our measured values for the $x=1.4$ sample (and $CeCu_2Si_2$) are $T_A=9$ K (12 K), $v_3=3.02(3.05)$, $a=4.144$ Å (4.098 Å), and $c=9.893$ Å(9.911 Å). Moreover, we noted that both of these two compounds are not magnetically ordered. Thus, we conjecture that this series should have developed into a HF system very similar to $CeCu_2Si_2$ at substitution level around $x=1.4$. A specific-heat measurement on this series would be very valuable for confirming this conjecture.

2. *Resistivity magnitude: x dependence*

In Fig. 6, we present the variation of the magnitude of the resistivity across the series at high ($T=260$ K) and low ($T=10$ K) temperature. Both of these $\rho(x)$ curves exhibit similar variation, i.e., a pronounced increase from $x=0.0$ to a maximum at $x=1.2$ (note however, the small drop from $x=0.6$ to 1.0 in the high-T $\rho(x)$ curve), followed by a large drop from $x=1.2$ to 2.0. This type of behavior has been observed a number of times before in some MV-Kondo systems such as $Ce(Pd,Ag)_3$, $Ce(Rh,Pd)_3B$, and $CeMn_2Si_{2-z}Ge_z$.[13,28,29] This type of behavior is typical of the following sequence: the resistivity in the Kondo regime rises rapidly as the mixed-valent regime is approached (in the present series from $x=2.0$ towards $x=1.2$); the resistivity peaks (at $x=1.2$ here) is quite close to but before the MV-Kondo borderline ($x=0.6$ here) is reached; and shortly after the MV regime is further approached and entered (i.e., below $x=0.6$) the resistivity drops sharply.

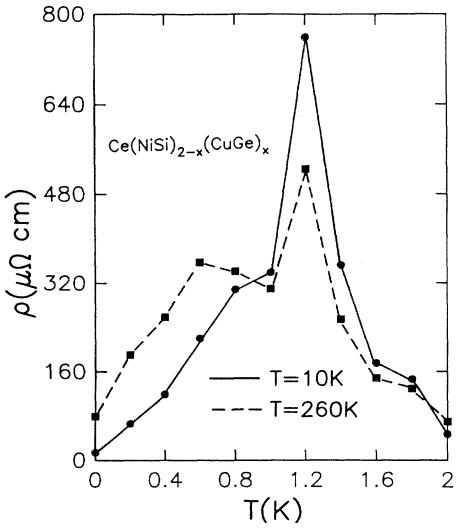

FIG. 6. The resistivity of polycrystalline samples of $Ce(NiSi)_{2-x}(CuGe)_x$ system at 10 and 260 K.

The high- and low-T $\rho(x)$ curves cross each other at $x\approx 0.9$ which separates the negative TCR from positive TCR regime in the series. At the peak location $x=1.2$, the value of the $\Delta\rho=\rho(260\text{ K})-\rho(10\text{ K})$ is most negative. This observation suggest that the strongest Kondo scattering occurs neither in the MV-Kondo borderline region (here at $x=0.6$) nor at the trivalent end (here at $x=2.0$), but someplace where the system is nearly trivalent (here at $x=1.2$ where $v_3=3.02$). Similar $\Delta\rho$ peaks have also observed in $CeMn_2Si_{2-z}Ge_z$, $Ce(Pd,Ag)_3$, and $Ce(Ru,Rh)_3B_2$ series at alloying concentrations at which v_3 is in the range of $3.02\le v_3\le 3.06$.[13,28-30] This suggestion is qualitatively consistent with some theories which predicted that the maximum scattering should occur when the energy of the $4f$ band E_{4f} is Δ (the half width of the $4f$ band) below the Fermi energy E_F.[31,32] With this E_{4f} (i.e., $E_F-\Delta$), the coupling constant $J=2V_{kf}^2|E_{4f}|/(E_{4f}^2+\Delta^2)$ is maximum and the $4f$ band is nearly fully occupied[31] (i.e., Ce is nearly trivalent). Quantitative estimate of the correlation between this E_{4f} and v_3 value relies on the availability of information such as the shape of the $4f$ band which may vary from one compound series to another.

3. *Coherence versus magnetic order*

The development of the low-temperature "coherence", i.e., the coherent coupling among the Kondo clouds centered at the Ce sites, is one of the most intriguing characteristics of Kondo lattice and heavy-fermion materials.[24] To distinguish the resistivity drop caused by coherence from that caused by magnetic order, we plot ρ/ρ_A versus T/T_A for four samples with $1.4\le x\le 2.0$ in Fig. 7. Here T_A and ρ_A are, respectively, the temperature and resis-

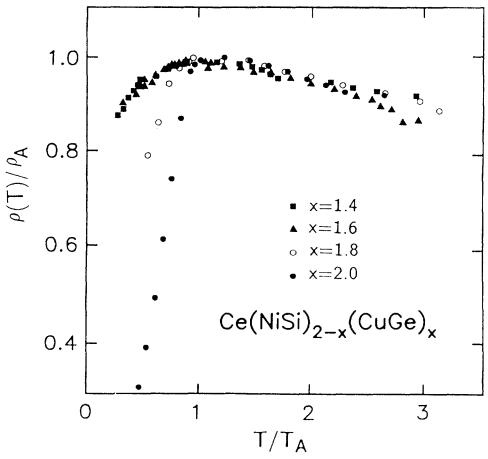

FIG. 7. The scaled resistivity $\rho(T)/\rho_A$ of the $x=1.4$, 1.6, 1.8, and 2.0 samples of $Ce(NiSi)_{2-x}(CuGe)_x$ system as a function of T/T_A. Here T_A and ρ_A are the temperature and resistivity of the resistivity maximum labeled by letter A in Figs. 4 and 5. Note the rounded behavior of the scaled resistivity for $x=1.4$ and 1.6 samples which supports the coherence interpretation. Note also the precipitous drop of the scaled resistivity for the $x=1.8$ and 2.0 samples, which supports the AF ordering interpretation.

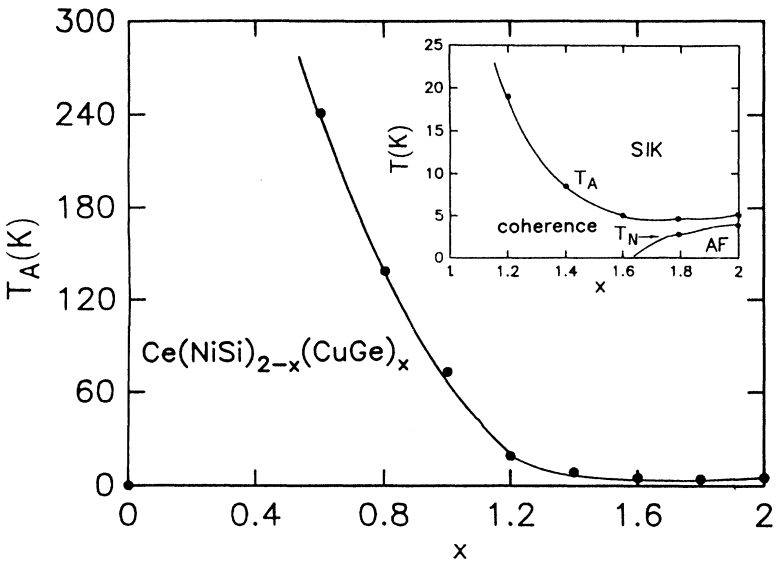

FIG. 8. The T_A vs x for $Ce(NiSi)_{2-x}(CuGe)_x$ series, where T_A is the temperatures corresponding to the resistivity maxima labeled by letter A in Figs. 4 and 5. The inset shows a phase diagram in which the $T_A(x)$ and $T_N(x)$ curves set the boundaries between the single-impurity Kondo (SIK), coherence, and antiferromagnetic (AF) regimes.

tivity values of peak A. Not like the $\rho(T)$ curves for other samples, the $\rho(T)$ curves of the $x=1.8$ and $x=2.0$ samples exhibit a very precipitous drop below T_A, indicating clearly the antiferromagnetic order. The magnetic ordering of the Ce $4f$ moments freezes the Kondo $4f$-spin scattering and causes sharp drops of the resistivity. On the other hand, the rough scaling behavior of the $\rho(T)/\rho_A$ curves for $T/T_A \leq 1$ for samples with $1.0 \leq x \leq 1.6$ is consistent with the coherency interpretation for these resistivities (to avoid crowding we have only shown the $x=1.4$ and 1.6 data in Fig. 7). This explanation is supported by the susceptibility results that the $x=1.6$ sample is not magnetically ordered down to $T=1.9$ K but that the $x=1.8$ sample is. It should be noted that this kind of scaling behavior below T_A has been previously observed for a number of Kondo-lattice systems such as $CeNi_{2-x}Cu_xSi_2$ and $CeMn_2Si_{2-z}Ge_z$ systems.[13,32]

It is observed in Fig. 7 that the T_A values for $x=1.8$ ($T_A=4.2$ K) and $x=2.0$ ($T_A=5.1$ K) do not match the corresponding T_N values ($T_N=2.41$ K for $x=1.8$ sample and $T_N=4.15$ K for $x=2.0$ sample). This indicates that the onset of the resistivity drop and the magnetic ordering of the Ce ions for present series do not occur at exactly the same temperature. Careful examination of the $\rho(T)$ data shows that the precipitous drop of the resistivity actually starts at $T=2.8$ K for $x=1.8$ and at $T=4.15$ K for $x=2.0$ samples, respectively (see also the inset of Fig. 5). These two temperatures are almost the same as the measured T_N values mentioned above. One often expects that T_N occurs where $d\rho/dT=$maximum in the absence of the complicating effects. For these two samples, the maximum values of $d\rho/dT$ are indeed observed at these two temperatures below which the $d\rho/dT$ is almost constant. The above observation indicates that for these two samples, there exists a coherence regime bounded by the $T_A(x)$ and $T_N(x)$ curves (see Fig. 8) which separates the single-impurity Kondo (SIK) from the antiferromagnetic (AF) ordered regime. These three regimes for the whole series are shown by the phase diagram in the inset of Fig. 8.

IV. CONCLUSION

This study shows that in $Ce(NiSi)_{2-x}(CuGe)_x$, the double (CuGe) for (NiSi) substitution smoothly drives the system from a highly mixed-valent system at $x=0.0$ into a magnetically ordered Kondo-lattice system at $x=2.0$. It is found that the physical properties of the $x=1.4$ material are very similar to that of the HF system $CeCu_2Si_2$. The present series spans the whole valence range of the Ce 1:2:2 compounds with v_3 ranges from 3.17 at $x=0.0$ to 3.00 at $x=2.0$. Combined $\rho(T)$ and $\chi(T)$ data indicate that the T_{sf} decreases continuously from $x=0$ to $x=2$, even though it is expected that the γ value should be peaked near $x=1.4$. The T_{sf} and Ce L_3-valence values for the $x>1.4$ samples have been shown to be smaller than that of $CeCu_2Si_2$.

We have clarified that the abnormal increase of the c parameter in the region $1.6 \leq x \leq 2.0$ is essentially independent of the Ce $4f$-ligand orbital dehybridization and thus this anomaly in the c parameter should be irrelevant to the HF character of these systems. The comparison between the resistivity and Ce L_3-valence data of the present series and the magnetic $3d$-host series $CeMn_2Si_{2-z}Ge_z$ strongly supports the proposal that a Kondo-type spin-fluctuation process can be effectively quenched by the strong internal magnetic field generated by the ferromagnetically ordered Mn sublattice.[13] The resistivity data also indicate that there is an active interplay between the crystalline electric field, coherence effect, single-impurity Kondo scattering (SIK), and magnetic ordering. Magnetic-susceptibility data show that this compound series is antiferromagnetically ordered for

$x > 1.6$, and the Kondo scattering and RKKY magnetic interaction are competitive in this region. Finally, a phase diagram is proposed to illustrate the evolution of the series successively from a SIK regime into a coherent Kondo regime (and then for larger x into an AF ordered regime) with the decreasing temperature.

ACKNOWLEDGMENTS

This work was supported by Research Corporation, Sam Houston State University Faculty Research Funds, and the National Science Foundation under Grant No. DMR-9158089.

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