

From intermediate valence to magnetic behavior without long-range order by hydrogenation of the ternary gallide CeNiGa

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We have studied both the crystal chemistry and magnetic, transport, and thermal properties of the hydride CeNiGaH_{1.1(1)}. This compound crystallizes in the hexagonal AlB₂-type structure with a random distribution of nickel and gallium atoms on the B site, which has an important influence upon the macroscopic properties. Its thermoelectric power versus temperature indicates that cerium is in a trivalent state. The electrical resistivity displays two minima, which could be expected for the Kondo-type interactions in the presence of crystal field effects. Specific heat measurements up to 300 K allow us to determine the splitting energies $\Delta_1=100$ K and $\Delta_2=159$ K. A broad maximum is observed around 4 K in the specific heat in the low temperature region. This maximum and its evolution with the applied magnetic field, are discussed in the framework of the existing theories, which point toward the existence of short-range magnetic correlations and spin glasslike freezing below 1.8 K. This study reveals: (i) that the hydrogenation of the intermediate valence gallide CeNiGa induces a valence transition for cerium which is purely trivalent in the hydride and (ii) the absence above 1.8 K of long-range magnetic ordering resulting from structural disorder around Ce atoms.

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I. INTRODUCTION

The use of extreme conditions is an important way to modify the physical properties of materials. Over the last few years, in addition to the low temperatures and high magnetic fields, the development of more performance pressure cells has made it possible to extend the use of high pressure and consequently to discover phenomena such as the coexistence of magnetism and superconductivity,¹ the appearance of quantum phase transition,² or the induction of magnetic order in a spin liquid compound.³ From this point of view, hydrogen insertion into the lattice can give rise to an important increase in the volume and therefore act as a negative chemical pressure which varies the properties in the materials.

In particular the hydrogenation of intermetallic compounds based on cerium is an interesting route in order to modify the competition between the Kondo effect and the magnetic Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction which governs their physical properties. This competition was explained using the magnetic phase diagram proposed by Doniach.⁴ The Kondo effect and RKKY interaction depend differently on the coupling constant J_{cf} between $4f(\text{Ce})$ and conduction electrons which is affected both by the $4f(\text{Ce})$ -conduction electrons mixing and the location of the $4f(\text{Ce})$ level E_{4f} relative to E_F Fermi level: (i) if E_{4f} is well separated to E_F , J_{cf} is small and the $4f(\text{Ce})$ electrons show a normal localized state with magnetic moments; (ii) when E_{4f} approaches E_F , J_{cf} increases and the compound begins to exhibit Kondo-like behavior (the magnetic ordering temperature and the magnetic ordered moment are reduced); (iii) when J_{cf} is increased even more, the compound goes into the nonmagnetic valence fluctuation regime. Considering this diagram, the hydrogenation can produce an interesting transition from a valence fluctuation ground state to a

magnetically ordered or even “heavy fermion” ground state. Indeed, the hydrogen insertion into the lattice generally induces an increase in the unit cell volume leading to a reduction in the coupling constant J_{cf} .

Recently, we have shown that the hydrogenation of the two CeNiGa crystallographic forms (LTF and HTF, respectively, for low and high temperature form) classified as intermediate valence compounds leads to the formation of the hydride CeNiGaH_{1.1(1)}.⁵ The synthesis of this hydride is accompanied by a large increase of the molar unit cell volume V_m ; respectively, +19.3% and +15.6% after hydrogenation of LTF and HTF. If we use a weighted average of the compressibility of the constituents elements in the solid state, as was done by de Visser *et al.*⁶ in the absence of data on the real compressibility, the increase in V_m from CeNiGa LTF corresponds to a negative pressure of $\cong -4$ GPa. Our preliminary characterization of CeNiGaH_{1.1(1)} by magnetization measurements suggests that the cerium is trivalent. In other words, the hydrogenation of CeNiGa induces a valence transition for cerium from the intermediate valence state (CeNiGa LTF and HTF) to a purely trivalent state (CeNiGaH_{1.1(1)}). Moreover, this hydride presents above 1.8 K no sign of any occurrence of a long-range magnetic ordering, suggesting perhaps a “heavy fermion” behavior. In order to solve this question, we have performed electrical resistivity, thermoelectric power, magnetoresistivity, and specific heat measurements on CeNiGaH_{1.1(1)}. It was found that below 4 K short magnetic correlations exist in this hydride. This behavior results from the statistical distribution of Ni and Ga atoms at the same crystallographic site and also the partial occupancy of the site devoted to H atoms. These structural properties induce some randomness in Ce-Ce exchange interactions. The results are discussed in relation to those reported on Ce₂NiGe₃ (Ref. 7) and Ce₂CuGe₃,⁸ which crystallize as

CeNiGaH_{1.1(1)}, in a derivative structure of the hexagonal AlB₂ type.

II. EXPERIMENTAL DETAILS

The polycrystalline samples of the ternary gallide CeNiGa and its hydride were synthesized and characterized by x-ray powder diffraction as previously described in Ref. 5.

For electron microscopy experiments (JEOL 2000FX), parts of the hydride CeNiGaH_{1.1(1)} were crushed in ethanol in an agate mortar and the small fragments were placed on a copper grid covered with an amorphous perforated carbon film.

For transport measurements, the hydride was compacted at room temperature (compactness $\cong 80\%$) in order to form a polycrystalline pellet (diameter=6 mm and thickness =3 mm) and then heated for two days at 523 K under pressure (5 MPa) of hydrogen. Thermoelectric power measurements were performed on this pellet using a dynamic method. Details of the cell used and measurement methods have been described previously.⁹ For electrical resistivity, a bar of $1.5 \times 1.5 \times 5$ mm³ was cut from the pellet. The measurement was carried out above 1.8 K using the standard dc four probe method with silver paint contacts and an intensity current of 10 mA. Magnetoresistivity research was performed down to 2 K for applied magnetic fields $0 \text{ T} \leq \mu_0 H \leq 9 \text{ T}$ on the same bar using the (PPMS) Quantum Design system. Finally, magnetization measurements were performed on a part of the pellet using a superconducting quantum interference device (SQUID) magnetometer in the temperature range 1.8–300 K and applied fields up to 5 T.

Heat capacity measurements on hydride CeNiGaH_{1.1(1)} were performed by a relaxation method with a Quantum Design PPMS system and using a two tau model analysis. Data were taken in the 2–300 K temperature range under applied magnetic fields of 0, 3, 6, and 9 T. For these latter measurements, the sample was a plate of 0.3 mm thickness and a 8.13 mg weight obtained from the same pellet used for the transport and magnetization measurements.

III. RESULTS AND DISCUSSION

Our investigation on the structural properties of the hydride CeNiGaH_{1.1(1)} using x-ray powder diffraction indicates that it crystallizes in the hexagonal AlB₂-type structure (space group *P6/mmm*) with $a=4.239(4)$ Å and $c=4.258(5)$ Å as unit cell parameters.⁵ In this structure, the Ni and Ga atoms are randomly distributed on the same crystallographic site; this distribution can be expected to cause some anomalous physical properties. For instance, the ternary germanides Ce₂NiGe₃ (Ref. 7) and Ce₂CuGe₃,⁸ which adopt the hexagonal AlB₂ type with a random distribution of Ni or Cu and Ge atoms, exhibit at low temperature a non-magnetic atom disorder spin glass behavior.

In order to confirm this crystal structure, we have examined some small crystals of this hydride by transmission electron microscopy. Typical electron diffraction patterns projected along the $[0 - 1 0]$ zone axis of the subcells of CeNiGaH_{1.1(1)} and CeNiSnH_{1.8(2)} are shown in Fig. 1. It can

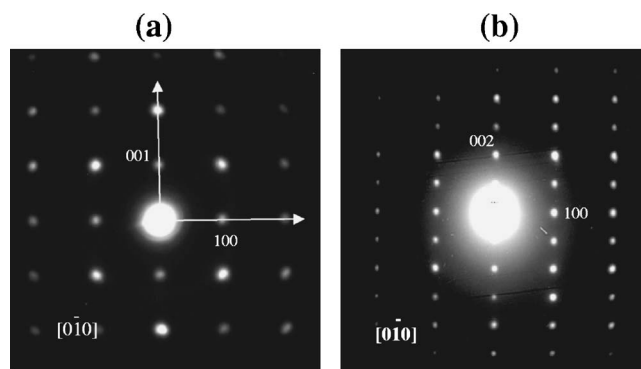


FIG. 1. Electron diffraction patterns of CeNiGaH_{1.1(1)} (a) and CeNiSnH_{1.8(2)} (b) along the $[0 - 1 0]$ direction.

clearly be ruled out that the lattice parameter $c=8.543(2)$ Å of CeNiSnH_{1.8(2)} is twice that corresponding to CeNiGaH_{1.1(1)}. The former hydride adopts the hexagonal ZrBeSi type, which is a variant of the AlB₂ type with an ordering of the Ni and Sn atoms.¹⁰ This atomic ordering induces the relation $c_{\text{ZrBeSi}}=2c_{\text{AlB}_2}$. The present study confirms the structural properties of the hydride CeNiGaH_{1.1(1)}. We note also that CeNiGaH_{1.1(1)} shows the same structural properties as the other hydride CeNiAlH_{1.93(5)},¹¹ but contains a much smaller hydrogen concentration. The partial occupancy of the crystallographic site devoted to the H atoms also induces structural disorder around the Ce atoms.

A. Magnetization

Above 100 K, the magnetic susceptibility χ_m of CeNiGaH_{1.1(1)} follows a Curie-Weiss law with $\theta_p=-100$ K as the paramagnetic Curie temperature and $\mu_{\text{eff}}=2.52 \mu_B/\text{Ce}$ as the effective moment.⁵ This last value is very close to that calculated for a free Ce³⁺ ion ($2.54 \mu_B$). Moreover, the large negative value of θ_p suggests that the Kondo effect plays an important role on the physical properties of this hydride.

At low temperatures, an interesting result is derived from comparing the temperature dependence of the magnetic susceptibility of CeNiGaH_{1.1(1)} measured in zero-field-cooled (ZFC) and field-cooled (FC) modes (Fig. 2). A small irreversibility effect appears below $T_{\text{IR}}=4$ K, but the absence of a peak above 1.8 K on the curve $\chi_{\text{ZFC}}=f(T)$ does not allow us to define a freezing temperature. Irreversibility is a typical feature expected for spin glasses.¹² In the same way, another characteristic of all the materials showing spin glass behavior is the remanence that can be observed when the applied magnetic field is changed below the irreversibility temperature T_{IR} . The inset of Fig. 3 shows the hysteresis of the magnetization of the hydride measured at 2 K; the remanence is about $0.001 \mu_B$ per Ce atom. The coercive field takes a small value close to 50 Oe. Finally, we note that the field dependence of magnetization at 2 K exhibits a curvature but is still not saturated at $\mu_0 H=5$ T (Fig. 3). All these results rule out the presence of long-range magnetic ordering for CeNiGaH_{1.1(1)}. Furthermore, although it exhibits some

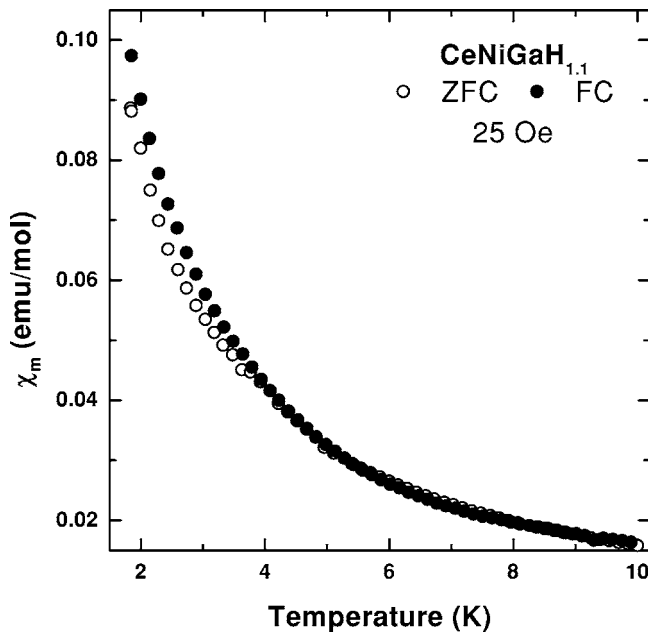


FIG. 2. Temperature dependence at $H=25$ Oe of the zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility of hydride $\text{CeNiGaH}_{1.1(1)}$.

typical features observed in spin glasses, the susceptibility shape does not resemble those commonly found in these materials; in addition, the ac susceptibility shows no peak at low temperature, as is always observed in spin glasses. These results suggest that the freezing temperature could be smaller than 1.8 K. Therefore, the irreversibility effect observed for this hydride might be interpreted in terms of short-range magnetic interactions dictated by crystallographic disorder.

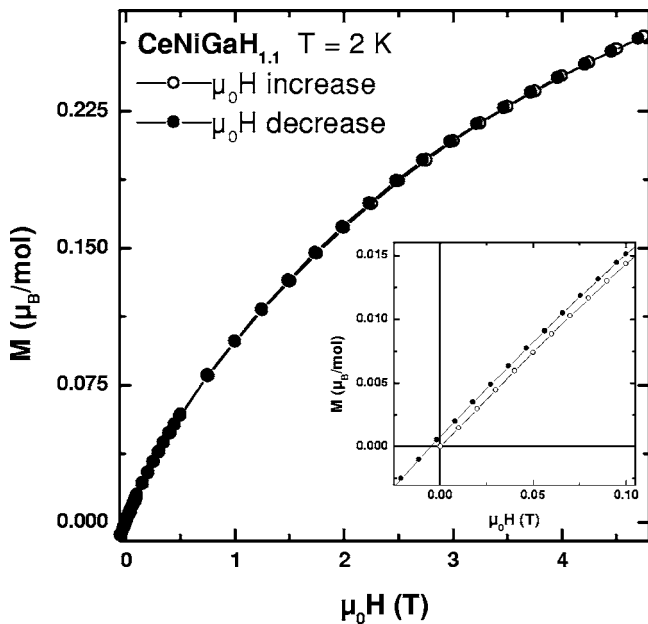


FIG. 3. Field dependence at 2 K of the magnetization of $\text{CeNiGaH}_{1.1(1)}$ measured with an increasing and decreasing applied magnetic field. Inset for the low magnetic field range.

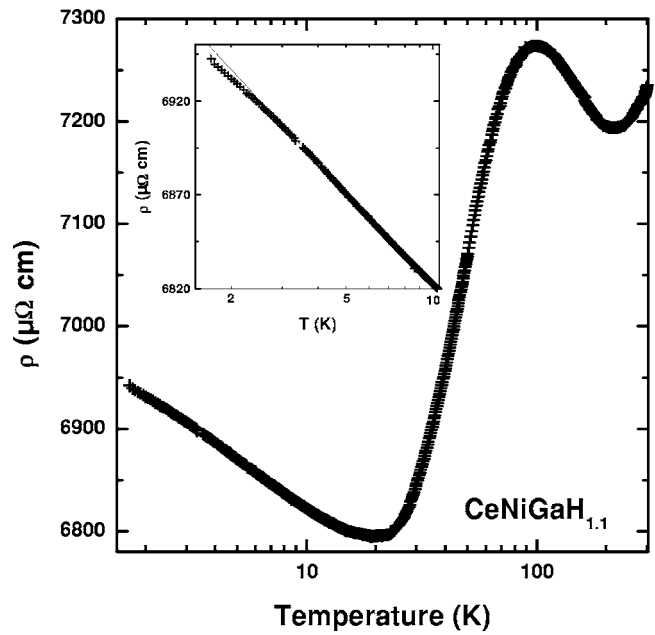


FIG. 4. Electrical resistivity as a function of $\log T$ for $\text{CeNiGaH}_{1.1(1)}$. The inset shows the temperature dependence for $T \leq 10$ K; the solid line represents the fit $-A \log T$.

B. Electrical resistivity and thermoelectric power

The temperature dependence of the electrical resistivity of $\text{CeNiGaH}_{1.1(1)}$ is depicted in Fig. 4. Before explaining its behavior and in order to understand it, we should make reference to the electrical resistivity measurements of CeNiGa LTF and HTF, which can be summarized as follows:⁵ (i) the curve $\rho=f(T)$ relative to CeNiGa LTF exhibits a quadratic temperature dependence between 4.2 and 70–75 K and then increases linearly with the temperature, which characterizes a nonmagnetic metal where the $4f(\text{Ce})$ electrons are strongly delocalized; the Kondo temperature T_K of CeNiGa LTF was estimated to be 1000 K; (ii) in contrast, the magnetic part of the electrical resistivity of CeNiGa HTF shows a broad maximum centered around 75 K as in the intermediate valence cerium compounds; in this case $T_K \approx 95(5)$ K was determined from the magnetic susceptibility measurements.

The electrical resistivity ρ of $\text{CeNiGaH}_{1.1(1)}$, exhibits a different behavior (Fig. 4). First, there is a large value of the residual resistivity $\text{RR}=\rho(1.8\text{ K})=6940\ \mu\Omega\text{ cm}$ and a small residual resistivity ratio $\text{RRR}=\rho(300\text{ K})/\rho(1.8\text{ K})=1.05$. Two hypotheses can be proposed in order to explain these values that are unusual for a normal metal; they can be attributed to (i) the presence of many porosities and microcracks resulting from the low temperature (523 K) used during the annealing treatment performed on the sample or (ii) the scattering due to the structural disorder as is usually observed in metallic spin glasses. It is interesting to note that the similar measurements performed on the hydrides $\text{CeNiSnH}_{1.0}$ and $\text{CeNiSnH}_{1.8}$ where Ni and Sn atoms are structurally ordered, give a higher RRR factor; 2.00 and 1.87 for $\text{CeNiSnH}_{1.0}$ and $\text{CeNiSnH}_{1.8}$ respectively.¹³ This comparison suggests that the electrical resistivity of $\text{CeNiGaH}_{1.1(1)}$ is strongly affected by the structural disorder

(Ni-Ga distribution and partial occupancy of the H site).

Interesting features can be observed on the curve $\rho(T) = f(\log T)$ relative to $\text{CeNiGaH}_{1.1(1)}$ (Fig. 4): (i) below 210 K, $\rho(T)$ increases with decreasing temperature up to a broad maximum appearing around 98 K; (ii) below this maximum, ρ decreases and a minimum occurs near 20 K; (iii) finally, below this minimum there is a rise of $\rho(T)$ down to 1.8 K. In the two temperature ranges 120–180 K and 3–10 K (inset of Fig. 4), the law $\rho(T) = -A \log T$ ($A = \text{constant}$) is observed. Such behavior is expected for Kondo-type interactions in the presence of crystal field effects.¹⁴ The high-temperature logarithmic region represents the Kondo effect in the excited doublet, whereas the low-temperature region is relative to the Kondo effect from the crystal field ground state. The maximum on the curve $\rho(T) = f(\log T)$ occurring between these two temperature ranges, is related to the crystal field splitting. We note that the temperature (98 K) of this maximum is close to that (100 K) where the curve $\chi_m^{-1} = f(T)$ deviates from the Curie-Weiss law.⁵ It is interesting to note that below 3 K, the resistivity deviates negatively from the law $\rho(T) = -A \log T$, suggesting the influence of magnetic correlations.

The curve $S = f(T)$ of the thermoelectric power plotted as a function of the temperature of the two crystallographic forms of CeNiGa and its hydride $\text{CeNiGaH}_{1.1(1)}$ are shown for the 4.2–300 K temperature range in Fig. 5. The two curves $S = f(T)$ relative to CeNiGa LTF and HTF are in agreement with their electrical properties. Below 300 K, the positive sign of S for the former implies that the dominant carriers are holes. For this ternary gallide, S decreases linearly from 28(1) to 8(1) $\mu\text{V}/\text{K}$ with the temperature between 300 and 90 K, takes a constant value in the temperature range 90–30 K and goes toward zero with decreasing temperature. This is the typical behavior of the valence fluctuating cerium compounds with a very high Kondo temperature as CeNi_2Si_2 ,¹⁵ CeNi_3 ,¹⁶ or $\text{Ce}(\text{Pd}_{0.85}\text{Rh}_{0.15})_3$.¹⁷ The curve $S = f(T)$ of CeNiGa HTF shows a clearly different behavior. It is mainly characterized by the existence of a positive maximum of about 10.5(5) $\mu\text{V}/\text{K}$ near 75 K and a shoulder around 20–30 K. This curve resembles that observed for CePd_3 which is well known as a canonical intermediate valence compound.^{18,19} The insertion of hydrogen into the CeNiGa lattice drastically changes the temperature dependence of its thermoelectric power (Fig. 5). At room temperature, S of $\text{CeNiGaH}_{1.1(1)}$ is close to zero. Also, the position of the maximum appearing on the curve shifts toward low temperatures (~ 40 K) and the absolute value of the maximum is reduced by a factor of almost two in comparison to the curve relative to CeNiGa HTF. Similar behavior was observed for the solid solution $\text{Ce}(\text{Pd}_{1-x}\text{Ag}_x)_3$ where the replacement of Pd by Ag induces a valence transition for cerium from the intermediate valence state (CePd_3) to a purely trivalent state $[\text{Ce}(\text{Pd}_{0.87}\text{Ag}_{0.13})_3]$.¹⁷ The evolution of the curves $S = f(T)$ in the sequence $\text{CeNiGa LTF} \rightarrow \text{CeNiGa HTF} \rightarrow \text{CeNiGaH}_{1.1(1)}$ is in agreement with the evolution of the valence of cerium (intermediate valence state \rightarrow trivalent state) deduced by magnetization measurements.⁵

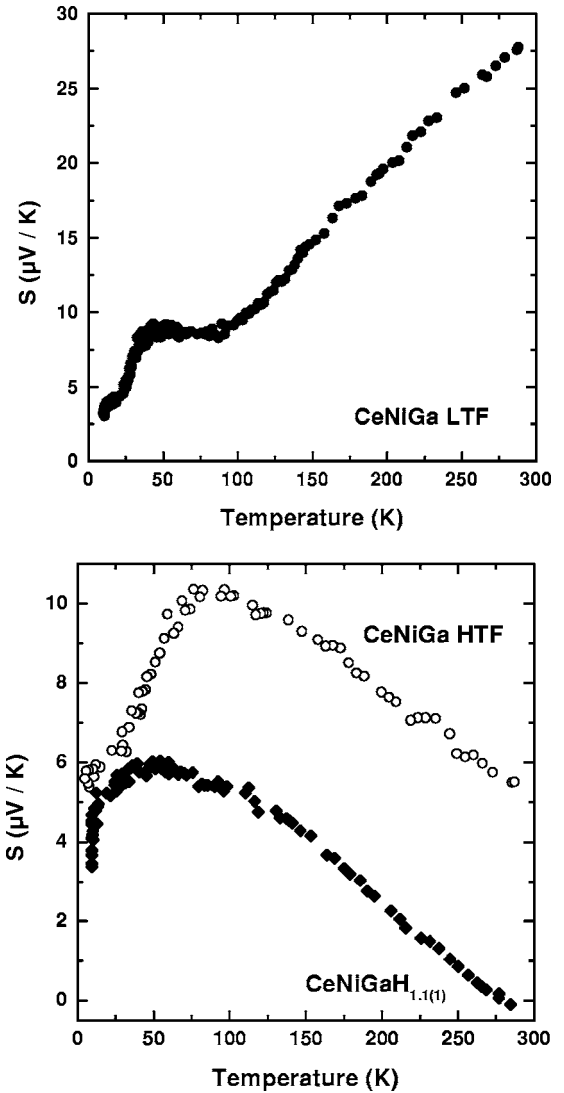


FIG. 5. Temperature dependence of the thermoelectric power for the ternary gallide CeNiGa LTF and HTF and its hydride $\text{CeNiGaH}_{1.1(1)}$.

C. Specific heat

The specific heat (C_p) of $\text{CeNiGaH}_{1.1(1)}$ has been measured at zero magnetic field between 2 and 300 K (Fig. 6). No λ -transition characteristic of magnetic order is observed anywhere along the whole temperature range. The increase of C_p with temperature is mainly due to the phonon contribution. In addition, we should have electronic and crystal field contributions. In the hexagonal system, as for this hydride, the sixfold degenerated $4-f$ state of Ce^{3+} ions ($J = 5/2$) splits into three doublets, with the excited states separated from the ground state by energy gaps Δ_1 and Δ_2 . In order to determine the splitting of the ground multiplet, the experimental $C_p(T)$ was fitted to the addition of three contributions

$$C_p(T) = C_{\text{el}}(T) + C_{\text{ph}}(T) + C_{\text{CEF}}(T).$$

(i) The electronic part $C_{\text{el}}(T) = \gamma_{\text{HT}} T$ was taken as linearly temperature dependent; (ii) in the absence of non- f -

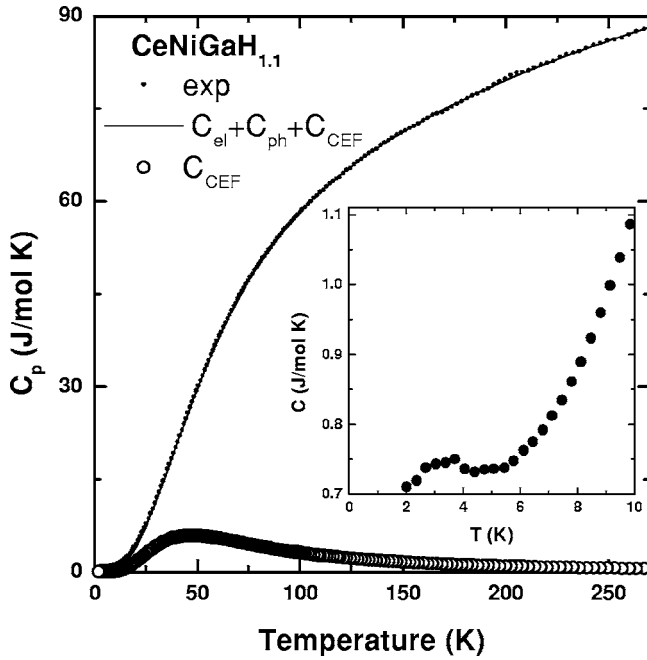


FIG. 6. Temperature dependence of the specific heat of $\text{CeNiGaH}_{1.1(1)}$ in a zero applied magnetic field. Experimental data (full points), fitting curve (full line), and contribution from the crystal electric field excitation (open circles). The inset shows the low temperature part for $T \leq 10$ K.

electron reference compound isomorphous to $\text{CeNiGaH}_{1.1(1)}$, the phonon contribution $C_{\text{ph}}(T)$ was assumed to follow a Debye model but, due to the important different weight of the constituents, we consider two different phonon spectra, each associated to a Debye temperature θ_D : $C_{\text{ph}}(T) = n_1 C_{\text{ph}}(\theta_{D1}) + n_2 C_{\text{ph}}(\theta_{D2})$ where $n_1 = 3$ corresponds to the number of atoms in the mol of CeNiGa and $n_2 = 1.1$ to that of H atoms by the mol of CeNiGa and $C_{\text{ph}}(\theta_D) = C_{\text{ph}}(T) = 9 R (T/\theta_D)^3 \int_0^{\theta_D/T} [x^4 e^x dx] / (e^x - 1)^2$; (iii) $C_{\text{CEF}}(T)$ is due to the crystal electric field effect:

$$C_{\text{CEF}}(T) = \frac{R}{(K_B T)^2} \times \frac{\Delta_1^2 e^{-\Delta_1/K_B T} + \Delta_2^2 e^{-\Delta_2/K_B T} + [\Delta_1 + \Delta_2]^2 e^{-(\Delta_1 + \Delta_2)/K_B T}}{[1 + e^{-\Delta_1/K_B T} + e^{-\Delta_2/K_B T}]^2}.$$

The best fitting between 25 and 300 K (see the continuous line in Fig. 6) is obtained for $\gamma_{\text{HT}} = 18$ mJ/mol K² as the Sommerfeld coefficient, $\theta_{D1} = 279$ K and $\theta_{D2} = 1223$ K as Debye temperatures and the contribution from the crystal electric field excitation to the specific heat (Fig. 6) gives the energy splitting $\Delta_1 = 100$ K and $\Delta_2 = 159$ K from the ground state, respectively. Although neutron diffraction experiments are necessary to check this (CEF) energy splitting scheme, we should stress that the fitting is very good (the fitted curve is over experimental points all along the entire temperature range) and the obtained values of the Debye temperatures and CEF splitting are quite reasonable. In fact, we note that according to Cornut and Coqblin,¹⁴ the high temperature maximum of the electrical resistivity (Fig. 4) takes place at a

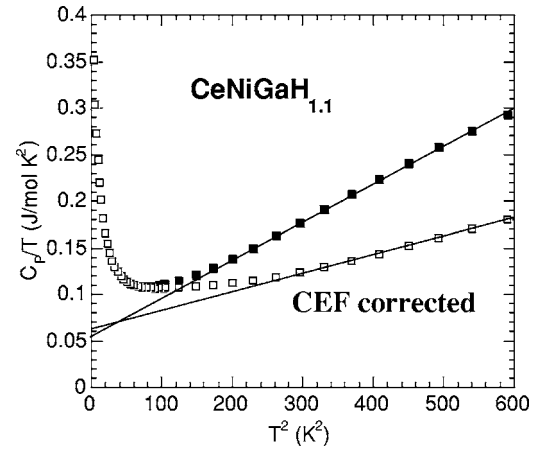


FIG. 7. The C_p/T versus T^2 $\text{CeNiGaH}_{1.1(1)}$ in $H=0$. Experimental data are plotted as filled squares (■), whereas the empty squares (□) have been obtained after subtracting the crystal field contribution. The lines represent fits to the data showing the γ_{LT} value, see text.

temperature slightly lower than that of the overall CEF splitting. In $\text{CeNiGaH}_{1.1(1)}$, the calculated value of $\Delta_1 = 100$ K is in rather good agreement with the temperature of the maximum (98 K) of $\rho = f(T)$ curve.

At low temperatures (see inset of Fig. 6), a very small and broad anomaly is observed near 4 K. This contains a very small amount of magnetic entropy of $S_{\text{mag}}/R = 0.10$ per Ce atom (corresponding to only 14% of the value $\ln 2$ expected for magnetic ordering of a crystalline-electric-field ground state doublet). This result excludes the occurrence of a long-range spatial magnetic ordering and indicates that the magnetic correlations are weaker. When we plot the specific heat in a C_p/T versus T^2 format (see Fig. 7), a linear region is observed above 13 K; therefore, we can obtain the electronic coefficient γ_{LT} by fitting the data to the formula $C_p/T = \gamma_{\text{LT}} + \beta_{\text{LT}} T^2$. The obtained values for the temperature range $13 \text{ K} < T < 23 \text{ K}$ were $\gamma_{\text{LT}} = 55$ mJ/mol K² and $\beta_{\text{LT}} = 0.412$ mJ/mol K⁴. Considering this value of γ_{LT} , we could define our hydride as a nonheavy fermion system; however, it is important to note that below 10 K, the C_p/T curve departs markedly from the linearity, reaching a large value of 352 mJ/mol K² at 2 K. Similar behavior was observed in many compounds considered as nonmagnetic atom disorder spin glasses.²⁰ For instance, the random distribution of boron in $\text{CePd}_3\text{B}_{0.3}$ introduces a varying electronic environment around the Ce atoms and causes an increase in C_p/T at low temperature.

To understand the origin of the very small and broad anomaly in the specific heat, we have analyzed the existing literature. In particular, a similar broad maximum in C_p was found in $\text{Ce}_x\text{Si}_{100-x}$ amorphous alloys around 4 K.²¹ In this case C_p/T also increases at low temperatures reaching large values (for example, 450 mJ/mol K² for $x=66$ samples). In addition, the magnetization increases by decreasing the temperature, without there being any signature of magnetic transition. This behavior was interpreted as being due to the atomic randomness which suppress the coherently ordered state such as degenerate Fermi liquid and the magnetic or-

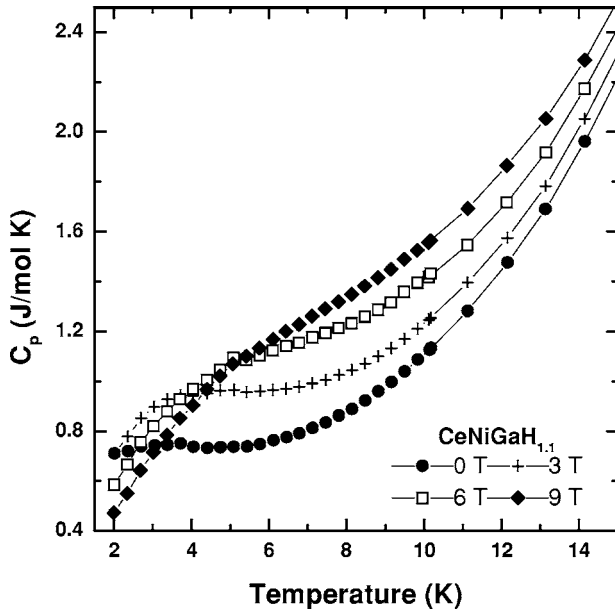


FIG. 8. Temperature dependence of the specific heat for $\text{CeNiGaH}_{1.1(t)}$ in different applied magnetic fields.

dered state observed in the crystalline counterparts. Further ZC-ZFC susceptibility measurements down to 1.8 K in the same $\text{Ce}_x\text{Si}_{100-x}$ amorphous family reveal the existence of spin glass transition around 2.5 K.²² From this point of view, we should remember that, according to Mydosh,¹² a broad transition at temperatures higher than the freezing one could appear in the heat capacity of spin-glasses.

The effects of the magnetic field on the C_p values in fields up to 9 T are shown in Fig. 8. We found that the magnetic field has a strong influence on the C_p values at low temperatures, its effects diminishing as the temperature increases, and being negligible above 25 K. The behavior is the following: below 25 K, C_p increases with the field, whereas at the lowest temperature C_p decreases, so the very broad maximum appearing on the curve of C_p at zero field moves to higher temperature with an increasing magnetic field. That means that the magnetic field transfers entropy from the lowest temperature region to the higher ones. This evolution of entropy with magnetic field is typical not only in ferromagnetic systems, but also in spin glass materials.¹² Indeed, in the previously mentioned $\text{Ce}_x\text{Si}_{100-x}$ amorphous compounds, the C_p peak position was found to shift to higher temperatures with the increasing magnetic field.²² Other compounds with similar behaviour are $\text{Ce}_{0.1}\text{Th}_{0.9}\text{Cu}_2\text{Si}_2$,²³ and Ce_2CuGe_3 (Ref. 8) and in both cases spin glass (or cluster glass) behavior was suggested as its origin. In particular, the last compound belongs to the family R_2TX_3 ($R=\text{U}, \text{Ce}$; T =transition metal and $X=\text{Ge}, \text{Si}$) in which the statistical distribution of T and X atoms at crystallographically equivalent lattice sites usually gives rises to random exchange interactions between R ions which favor the apparition of spin glasses behavior.⁷ In our case, it is worth mentioning that in addition to the disorder between Ni and Ga atoms, there is a random distribution of the hydrogen position inside the lattice, which certainly increases the randomness of (i) the exchange interactions and (ii) the local magnetic anisotropy,

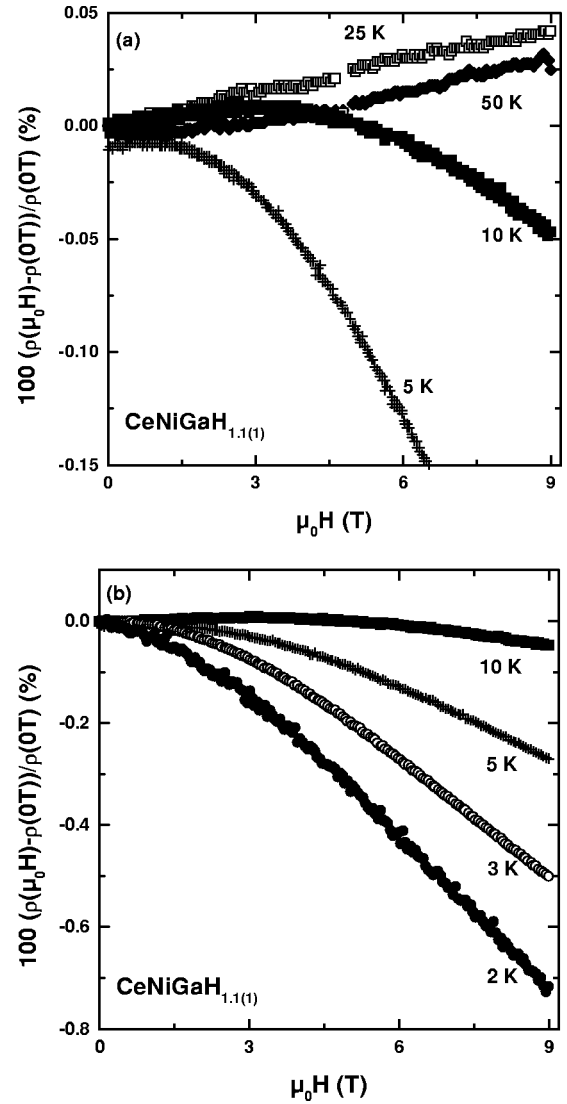


FIG. 9. Field dependence of magnetoresistivity for $\text{CeNiGaH}_{1.1(t)}$ in the temperature range $5 \text{ K} \leq T \leq 50 \text{ K}$ (a) and $2 \text{ K} \leq T \leq 10 \text{ K}$ (b). The dotted lines are relative to the fit with $-a(\mu_0 H)^2$ expression.

thereby provoking the occurrence of the spin glass behavior at low temperatures.

Therefore, in view of the different models which could account for our specific heat and its evolution with magnetic field, and discarding the existence of a long-range magnetic order, the most likely explanation is the following: magnetic correlations or even short-range magnetic order emerge by decreasing the temperature below 4 K as a previous state of the spin glass freezing which occurs below $T_f < 1.8 \text{ K}$. A similar scenario is that paramagnetic random magnetic moments correlate to form magnetic clusters below 4 K and those magnetic clusters are frozen in a cluster glass phase below T_f , losing their dynamical aspect. In both cases, the existence of short-range magnetic order prior to the freezing process could explain both the occurrence of small irreversibility in the susceptibility below 4 K and the small anomaly in C_p .

Our last comment is about the γ_{LT} coefficient which, although not large enough to consider CeNiGaH_{1.1} as a heavy fermion, is one order of magnitude larger than the expected in the free electron model. In this sense, Gschneidner *et al.*²⁰ indicate that large C_p/T values may mislead one to classify a spin glass within a heavy fermion system. In fact, they pointed out that the possible mechanism that will enhance the C_p/T values are (i) low lying crystal fields levels, (ii) a spin glass phase, and (iii) magnetic order at low temperature. Because point (iii) is already discarded, we proceeded to investigate the influence of the crystal field. We subtracted from the total heat capacity the CEF contribution previously determined and then used these data to recalculate γ_{LT} . Because $\Delta_1=100$ K is relatively larger, the CEF subtraction primarily reduces the slope of the specific heat curve and consequently enhances the γ value in a C_p/T versus T^2 representation (see Fig. 7). Therefore the CEF corrected value $\gamma_{LT}=61$ mJ/mol K² is even higher than the uncorrected one (55 mJ/mol K²) as was also determined in CePb₃.²⁴ This observation discards point (i) as well, and thus supports the existence of a spin glass transition as the origin of the large C_p/T values at low temperatures.

D. Magnetoresistivity

Figure 9 shows at different temperatures the magnetoresistivity (MR) defined by $[\rho(\mu_0H)-\rho(0\text{ T})]/\rho(0\text{ T})$ as a function of applied magnetic fields for CeNiGaH_{1.1(1)}. Above 25 K, MR is small, always positive, and increases with decreasing temperatures; for $\mu_0H=9$ T, MR is equal to +0.03% and 0.04% at $T=50$ and 25 K respectively. This behavior indicates that the Kondo effect is so weak in this temperature range that MR is dominated by the positive contribution arising from the influence of μ_0H on the conduction electrons. At $T=10$ K, MR is positive at low fields, passes through a maximum near $\mu_0H=3$ T, and changes in sign around $\mu_0H=5$ T. Below 10 K, MR is always negative and its magnitude increases with decreasing temperatures; MR measured at $\mu_0H=9$ T is about -0.27%, -0.50%, and -0.73% for $T=5$, 3, and 2 K, respectively. In this temperature range $T < 10$ K, the negative MR is due to the freezing out of spin-flip scattering in a Kondo compound by the magnetic applied field. We have fitted the data [Fig. 9(b)] with an $-a(\mu_0H)^2$ law usually appearing in Kondo systems. At $T=5$ K, a quadratic field dependence is observed at least up to $\mu_0H=9$ T;

the constant value a is equal to $3.39 \cdot 10^{-3} \% T^{-2}$. Below $T=5$ K, the range over which the $-a(\mu_0H)^2$ dependence holds decreases as the temperature is lowered; for instance at 3 and 2 K, this law is respectively, followed for $(\mu_0H) < 5.9$ T and $(\mu_0H) < 3.2$ T. These deviations indicate for $T < 5$ K the influence of magnetic correlations. This study confirms the presence of Kondo fluctuations in CeNiGaH_{1.1(1)} which influences its magnetoresistivity below $T < 10$ K.

IV. CONCLUSION

The hydride CeNiGaH_{1.1} crystallizes in the hexagonal AIB₂-type structure with a random distribution of nickel and gallium atoms on the B site. Moreover, the partial occupancy of the crystallographic site devoted to the H atoms also induces structural disorder around the Ce atoms. The magnetization, electrical resistivity, specific heat, and magnetoresistivity measurements presented here confirm that this hydride does not show detectable long-range magnetic ordering down to 1.8 K. But this study reveals some characteristic features of nonmagnetic atom-disorder spin glasses: (i) a small irreversibility effect appears below 4 K in the thermal dependence of its magnetization; (ii) its electrical resistivity deviates negatively below 3 K from the law $\rho(T)=-A \log T$ suggesting the presence of magnetic correlations; (iii) near 4 K, a broad maximum is detected on the curve $C_p=f(T)$; this maximum moves to a higher temperature with an increasing magnetic field; and (iv) finally, at low temperatures, its magnetoresistivity results from a competition between the Kondo effect and the magnetic correlations. Heat capacity up to room temperature allows us to determine the Schottky-type anomaly associated to the ground multiplet of Ce³⁺ ions ($J=5/2$). These results confirm that the negative pressure produced by hydrogen insertion in CeNiGa induces a change from intermediate valence to a trivalent state in the Ce ions and gives rise to the appearance of spin glass behavior at low temperatures.

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