Large anisotropic thermal expansion and magnetostriction in the mixed-valence compound CeNi

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We present thermal-expansion and magnetostriction measurements performed at low temperature along the three symmetry axes of the orthorhombic intermediate-valence compound CeNi. The field effects are interpreted as the sum of a main contribution arising from the intermediate-valence character, which is temperature independent, and a smaller one whose temperature and field dependences are characteristic of Ce^{3+} impurities. The low-temperature thermal expansion and the main contribution to the magnetostriction are large and strongly anisotropic. The volume effects, which are larger than in the $CeSn_3$ reference intermediate-valence compound, are interpreted within a T/T_f scaling-law model (T_f being the fluctuation temperature) which predicts the observed temperature dependence of the thermal expansion and field dependence of the magnetostriction. The strong anisotropy, especially the unusual negative thermal expansion and perpendicular magnetostriction along $\hat{\mathbf{b}}$ must be related mainly to the local elastic properties in which the covalent character of the $4f$-$5d$-$3d$ hybridization between Ce and Ni could play a predominant role.

I. INTRODUCTION

In mixed-valence compounds the $4f$ instability leads to strong electron-lattice coupling. Consequently, the space parameters are strongly related to the intermediate-valence character, so that the elastic properties are of first importance in the understanding of such systems. These effects can be studied either from the pressure dependence of some physical properties (like specific heat, susceptibility, etc.) or from direct lattice-parameter measurements (thermal expansion, magnetostriction, etc.), these two experimental approaches being thermodynamically equivalent as shown by the classical Maxwell relations.

Such a study has been performed in cubic compounds like $CeSn_3$ and $CePd_3$ from specific heat,[1] thermal-expansion[1], elastic constant,[1] and magnetostriction[2] measurements. Takke *et al.*[1] have discussed these results using a phenomenological scaling function for the free energy, the electron-lattice coupling being described by an electronic Grüneisen parameter associated with the unstable $4f$ system. However, these calculations did not include the volume self-consistently. Later Edelstein and Koon[3] employed the resonant-level model in which they incorporated the coupling to the volume in a completely self-consistent manner. Because of the cubic symmetry, no anisotropy of the observed physical properties was detected, and hence the volume is the only relevant parameter in such systems.

It has been previously shown that the CeNi compound is one of the best examples of an intermediate-valence system where the low symmetry leads to strong anisotropic effects.[4] Indeed, CeNi crystallizes in the Cr*B*-type orthorhombic structure (space group *Pnma*), and lattice-parameter analysis as well as thermal expansion show that it is, like $CeSn_3$, an intermediate-valence compound in which the thermal dependence of the $4f$-$5d$-$3d$ hybridization between Ce and Ni leads to an increase of the $4f$ localization as temperature is increased. Magnetic susceptibility, resistivity, and heat-capacity measurements are characteristic of a Fermi liquid in which spin fluctuations are present. Moreover, CeNi behaves as an enhanced Pauli paramagnet in which the magnetic susceptibility passes through a broad maximum around the so-called fluctuation temperature $T_f \simeq 140$ K (Fig. 1). However, the origin of the low-temperature $1/T$ increase of the observed initial susceptibility[5] remains an open question. This problem is formally the same as in $CeSn_3$ where the susceptibility has been much more investigated in terms of its intrinsic or impurity origin.[6] We have studied the electron-lattice coupling associated with the $4f$ instability in CeNi by thermal expansion and magnetostriction measurements on a single crystal at temperatures well below T_f.

II. EXPERIMENTAL RESULTS

Thermal expansion and magnetostriction in fields up to 70 kOe (parallel to the measuring direction) or 40 kOe (perpendicular) were measured using a classical capacitance technique. The single crystals were prepared by the Bridgman technique, using 99.99% pure cerium to avoid any additional impurity effects. In order to subtract the background effect, a single crystal of LaNi was also prepared and measured in the same conditions as those used in the previous susceptibility measurements.[4,5]

In Fig. 2 we present thermal-expansion data

$$\epsilon_\lambda(T)=\frac{\lambda(T)-\lambda(T=0)}{\lambda(T=0)} \quad \text{for } \lambda=a,b,c ,$$

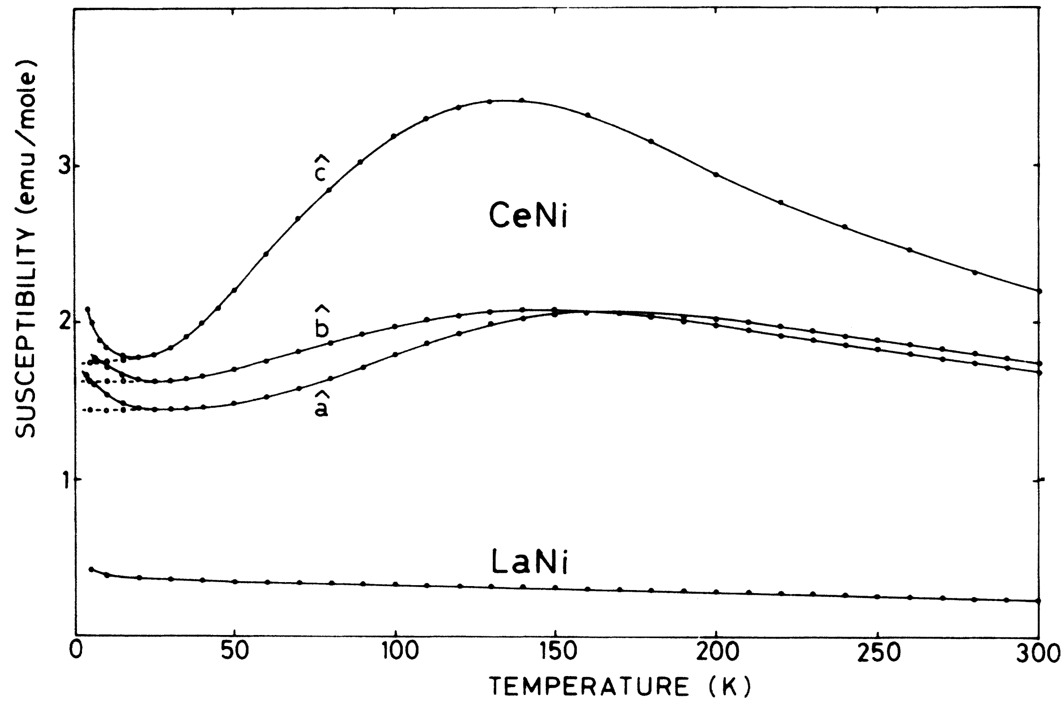

FIG. 1. Thermal variations of the susceptibilities of CeNi in zero field (—•—) and in a 40-kOe field (- - ∘ - -) along the three symmetry axes of the orthorhombic structure. Above 25 K the susceptibility in zero field is the same as in a 40-kOe field. Thermal variation of the initial susceptibility of a polycrystalline sample of LaNi (—•—).

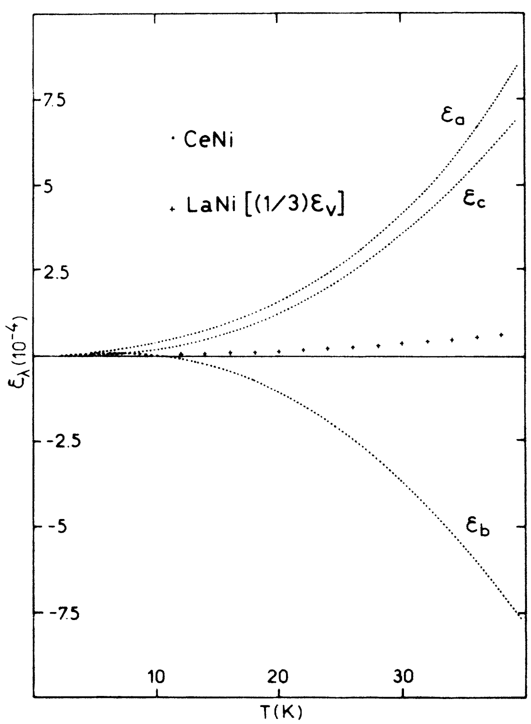

FIG. 2. Low temperature thermal expansion of CeNi along the three symmetry axes and of the reference LaNi compound [only small differences are observed in this compound between the three axes; hence, for clarity we trace $\frac{1}{3}\epsilon_v=\frac{1}{3}(\epsilon_a+\epsilon_b+\epsilon_c)$].

for CeNi and LaNi below 40 K. In this range of temperature, and within the experimental accuracy, we observe only small differences between the three axes in the background LaNi compound. The main characteristics of these thermal expansion measurements are the following:

(i) The effects in CeNi are very large with respect to those measured in LaNi and, more generally, with respect to most solids at low temperature.[7] As shown previously,[4] these effects are associated with the intermediate-valence character.

(ii) Large anisotropy is observed: while ϵ_a and ϵ_c are positive and very similar, ϵ_b is very weak up to 12 K (due to the background positive contribution) and then negative and of the order of magnitude of the others.

(iii) If we subtract the LaNi effects, we obtain for $T<20$ K quite accurate T^2 variations along the a and c axes, i.e., linear variations for the thermal expansion coefficients

$$\alpha_\lambda=\frac{d\epsilon_\lambda}{dT}(\text{CeNi})-\frac{d\epsilon_\lambda}{dT}(\text{LaNi}) ,$$

the values of α_a/T and α_c/T being, respectively, $0.63\times10^{-6}\ \text{K}^{-2}$ and $0.40\times10^{-6}\ \text{K}^{-2}$. Along the b axis up to 12 K, the negative contribution due to the intermediate-valence character is weak and of the same order of magnitude as the positive background one. For this reason it is difficult to extract a significant value for the coefficient α_b/T. However, it is possible to say, for $T \ll T_f$, that this coefficient is weak and negative, rang-

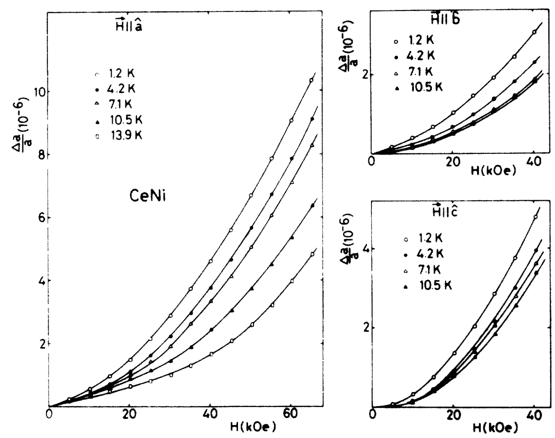

FIG. 3. Parallel and perpendicular magnetostriction of CeNi along the a axis at different temperatures below 23 K.

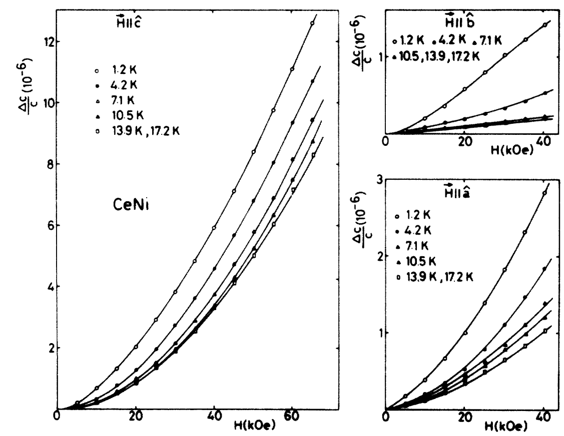

FIG. 5. Parallel and perpendicular magnetostriction of CeNi along the c axis at different temperatures below 23 K.

ing between -0.02×10^{-6} and -0.09×10^{-6} K^{-2}.

(iv) Subtracting the LaNi contribution we obtain for $T<30$ K a T^2 variation of the volume expansion ϵ_v, i.e., a linear variation for the volume thermal-expansion coefficient $\alpha_v=\alpha_v(\text{CeNi})-\alpha_v(\text{LaNi})$, leading to $\alpha_v/T=0.64\times10^{-6}$ K^{-2}.

The magnetostrictions

$$\epsilon_\lambda(\mathbf{H}//\hat{\mu})-\epsilon_\lambda(H=0)\frac{\Delta\lambda(\mathbf{H}//\hat{\mu})}{\lambda(H=0)}$$

along each axis ($\lambda=a,b,c$) were measured for fields applied alternatively along these three directions ($\mu=a,b,c$). The data are reported in Figs. 3–5. The main points of these results are the following:

(i) All the variations are almost temperature independent in the region between 23 K (maximum measured temperature) and 14 K, and exhibit an H^2 dependence in this region. However, when temperature is decreased below 14 K we observe a more or less pronounced increase of the effects. We can already relate this thermal variation at low temperature to the $1/T$ increase of the susceptibility in the same temperature region reported previously;[5] this point will be discussed in detail in the next section.

(ii) While for all directions the parallel magnetostriction is positive, the b axis, as for thermal expansion, exhibits special behavior for the perpendicular magnetostriction which is negative for the two directions of the field ($\hat{a}$ and $\hat{c}$), whereas it is positive for ϵ_a and ϵ_c in perpendicular fields.

(iii) We also measured the magnetostriction of LaNi in the same conditions and we obtained effects negligible with respect to the CeNi effects.

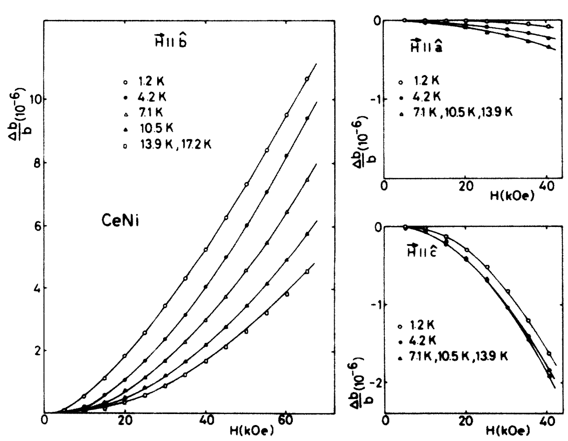

FIG. 4. Parallel and perpendicular magnetostriction of CeNi along the b axis at different temperatures below 23 K.

III. ANALYSIS AND DISCUSSION

The $4f$ instability in CeNi leads to large and strongly anisotropic effects on thermal expansion and magnetostriction. The volume effects are especially higher than in the cubic $CeSn_3$ compound which is one of the reference intermediate-valence systems. Indeed, the ratio $[\alpha_v(CeSn_3)-\alpha_v(LaSn_3)]/T$ is 0.23×10^{-6} K^{-2}, whereas it is 0.64×10^{-6} K^{-2} in CeNi. Also, at 14 K the volume magnetostriction $\Delta V/V$ of CeNi in a 40-kOe applied field is 1.98×10^{-6}, 3.63×10^{-6}, and 4.23×10^{-6} when the field is applied along $\hat{a}$, $\hat{b}$, and $\hat{c}$, respectively, whereas it reaches only 0.56×10^{-6} under the same conditions in $CeSn_3$.

The thermal variation of the magnetostriction below 14 K cannot be interpreted solely by valence-fluctuation effects, because a temperature dependence of the magnetostriction needs a correlated temperature dependence of the susceptibility, which is not the case in this range of temperatures (see Fig. 1). Since the magnetostriction is temperature independent between 14 and 23 K, we assume that it represents the intrinsic contribution due to the valence-fluctuation effects in the whole temperature range below 23 K. The extra contribution to the magnetostriction along the c axis is reported as a function of the applied field at different temperatures in Fig. 6. We clearly observe linear field dependences and a classical decrease as temperature is increased. The same characteristics are observed for the extra contribution to the other directions of measurement. It is possible to make a quantitative

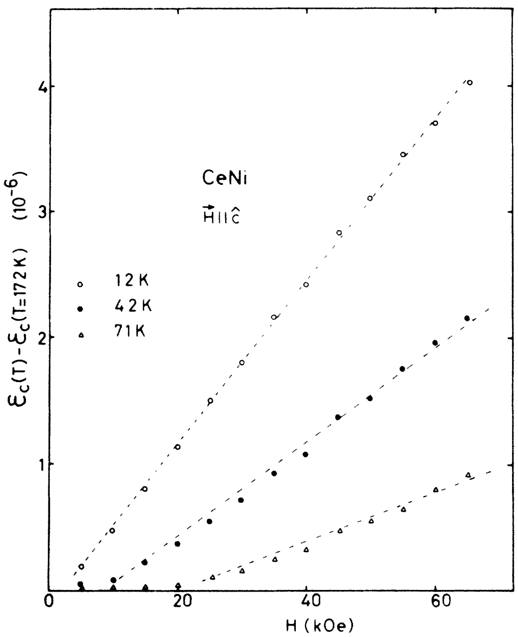

FIG. 6. Low-temperature extra contribution to the parallel magnetostriction along the c axis.

analysis of this extra contribution based on the magnetoelastic coupling between magnetic Ce^{3+} ions and the surrounding lattice, similar to those analyses performed on cubic hexagonal dilute rare-earth alloys.[8] Such an effect can be also associated with a $1/T$ increase of the initial susceptibility at low temperature of these magnetic ions, according to the deviations observed previously (see Fig. 1).[5] This coherent interpretation of the two deviations in susceptibility and magnetostriction at low temperature tends to eliminate an intrinsic origin of similar low-T susceptibility effects which have already been observed in several isotropic intermediate-valence compounds.[6] By comparison with dilute alloys, we can evaluate the concentration of the Ce^{3+} impurities to be around 0.5%. Finally, we have to note that, again by comparison with dilute alloys, the influence of these impurities on the thermal expansion is about two orders of magnitude smaller than the total observed effects which can be solely attributed to intermediate-valence fluctuations.

The intrinsic part which corresponds to the variations observed between 14 and 23 K exhibits H^2 dependence for the volume magnetostriction as well as for the magnetostriction along each axis up the the maximum applied field (let us remark that such a law is a general rule around zero field as a consequence of the invariance in time inversion). This gives rise to M^2 variations as observed in $CeSn_3$; however, in CeNi the M^2 dependence of the volume magnetostriction when the field is applied along $\hat{c}$, for example, is around ten times greater than in $CeSn_3$. Let us now try a more quantitative analysis of our results.

A. Volume effects

As mentioned above, intermediate-valence compounds such as $CeSn_3$ and CeNi exhibit strong charge and spin fluctuations which are maximum around the so-called fluctuation temperature T_f, which defines an approximate scaling temperature such that the properties can be expressed as a function of T/T_f. Takke *et al.*[1] have proposed writing the electronic and the electron-lattice contributions for the free energy of an intermediate-valence compound as

$$F_e=-kTNf(T/T_f)\ , \tag{1}$$

where N is the number of $4f$ ions per unit volume.

The volume effects are governed by a Grüneisen parameter associated with the unstable $4f$ shell

$$\Omega_g=\frac{-\partial \ln T_f}{\partial \epsilon_v}\ . \tag{2}$$

Following Takke *et al.*,[1] we can write for low temperature ($T \ll T_f$) the electronic parts of the specific heat

$$C_e=-T\frac{\partial^2 F_e}{\partial T^2}=Nk\frac{T}{T_f}\left[2f'+\frac{T}{T_f}f''\right] \tag{3}$$

and the volume thermal-expansion coefficient

$$\alpha_e=-\frac{1}{C_B}\frac{\partial^2 F_e}{\partial T\partial \epsilon_v}\simeq\frac{\Omega_g Nk}{C_B}\frac{T}{T_f}\left[2f'+\frac{T}{T_f}f''\right]\ , \tag{4}$$

where C_B is the bulk modulus which appears in the elastic free energy $F_{el}=\frac{1}{2}C_B\epsilon_v^2$. The well-known classical relation

$$\alpha_e=C_e\frac{\Omega_g}{C_B} \tag{5}$$

is obtained simply from (3) and (4), and is generally used to derive the Grüneisen parameter from heat-capacity and thermal-expansion experiments.

In order to include the effect of a magnetic field on a mixed-valence system within this model, Takke *et al.* proposed replacing T/T_f by $[T^2+(\mu^2H^2/k^2)]^{1/2}/T_f$ in (1) for $\mu H \ll kT$. The following expressions are obtained, in the case of isotropic magnetic effects, for the susceptibility

$$\chi=\frac{N\mu^2}{kT_f}f' \tag{6}$$

and volume magnetostriction

$$\epsilon_v(H)-\epsilon_v(0)=\frac{\Omega_g\chi}{C_B}\frac{H^2}{2}\ . \tag{7}$$

From (3) and (6) one finds for the low-temperature ratio, $T\chi/C_e=\mu^2/2k^2$.

Despite the fact that in an anisotropic system like CeNi the volume expansion ϵ_v is not a relevant parameter, i.e., Ω_g must be replaced by three Grüneisen parameters $\gamma_\lambda=-\partial \ln T_f/\partial \epsilon_\lambda$, with $\lambda=a,b$, and c; we can perform a first-order analysis of the volume effects using this isotropic scaling approach. Indeed, we observed a T^2 dependence for the volume thermal-expansion and H^2 dependences for the volume magnetostriction (Fig. 7). Moreover, taking into account the anisotropy of the susceptibility (see Fig. 1), the coefficients of these H^2 variations are

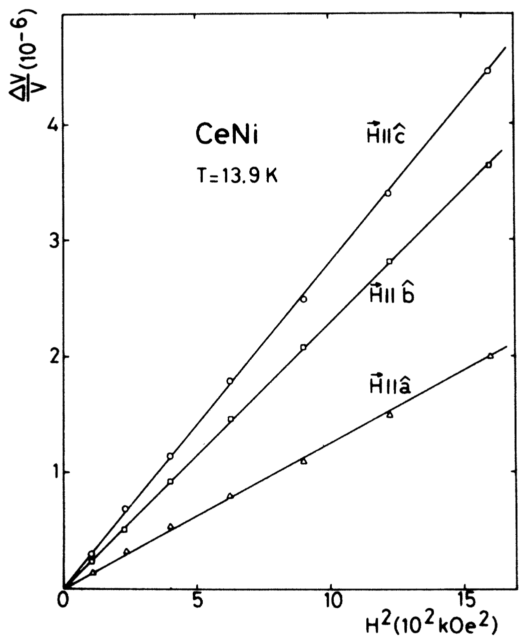

FIG. 7. Volume magnetostrictions of CeNi at 13.9 K as a function of H^2 for the field applied along the three symmetry axes.

clearly of the same order as the susceptibilities as implied by (7). Trying to make a quantitative comparison, we can deduce from (5) the Grüneisen parameter Ω_g using the electronic heat capacity previously measured.[4] The bulk modulus C_B is estimated to be around 2.8×10^{11} erg cm^{-3} form recent elastic constant measurements,[9] using $C_B=\frac{1}{9}[C_{11}+C_{22}+C_{33}+2(C_{12}+C_{23}+C_{31})]$ for orthorhombic symmetry. We obtain a value $\Omega_g\simeq8$ which is a little smaller than that deduced for $CeSn_3$ at low temperature ($\simeq10$).

From these values of Ω_g and C_B and from the measured susceptibilities, we can deduce the three coefficients $\Omega_g\chi_\lambda/2C_B$ which appear in (7) for fields applied along the three symmetry axes ($\lambda=a,b,c$). While we then obtain (in units of $10^{-15}Oe^{-2}$), respectively, 0.80, 0.89, and 0.91, the measured values (see Fig. 7) are 1.25, 2.27, and 2.78. This discrepancy clearly shows the limits of the model, especially for the introduction to the field effects although it seems to be rather valid for thermal effects.

B. Anisotropic effects

As observed, anisotropic effects are expected in CeNi due to the orthorhombic symmetry. However, the negative thermal expansion and the negative perpendicular magnetostriction measured along $\hat{b}$ are unusual in Ce-based intermediate-valence compounds. Indeed, when temperature is increased, the intrinsic volume expansion which corresponds to that observed in LaNi is enhanced by the localization of the 4f electrons. Also, a magnetic field introduces a negative magnetic contribution to the free energy whose minimization is obtained by increasing this contribution. This can be done by localizing the 4f electrons and then by increasing the volume. The reason for this special behavior of the b axis magnetostriction, which is not yet clear, may be associated with the local packing of the atoms in which a covalent character of Ce-Ni hybridization would play a dominant role.

In an attempt to account phenomenologically for the observed anisotropy, we have extended the scaling model to orthorhombic symmetry, where $T_f(\epsilon_a,\epsilon_b,\epsilon_c)$ depends on the strains ϵ_a,ϵ_b, and ϵ_c in a different way, leading to three Grüneisen parameters

$$\gamma_\lambda=-\frac{\partial\ln T_f}{\partial\epsilon_\lambda}\ , \tag{8}$$

where $\lambda=a,b,c$ and $\epsilon_\lambda=\Delta\lambda/\lambda$.

Following Barron *et al.*[7] we write the elastic part of the free energy as

$$F_{el}=\sum_{\lambda,\mu}\tfrac{1}{2}C_{\lambda\mu}\epsilon_\lambda\epsilon_\mu\ , \tag{9}$$

where we introduce the elastic constants $C_{\lambda\mu}$. Minimizing the total free energy, we deduce easily the extension of (5) to the anisotropic case

$$\alpha_\lambda=C_e\sum_\mu S_{\lambda\mu}\gamma_\mu\ , \tag{10}$$

where the α_λ are the linear thermal-expansion coefficients along each λ axis, and the $S_{\lambda\mu}$ are the compliances which belong to a tensor which is the inverse of the elastic constant tensor. Restricting to thermal effects, it is possible to estimate the three Grüneisen parameters γ_a, γ_b, and γ_c from the experiment: in the low-temperature region we obtain 13.7, 2.3, and 10.0, respectively. However, this result must be considered with caution because such an extension of the scaling approach to the anisotropic case must also give a qualitative and quantitative analysis of the field effects. Unfortunately, the expressions derived in a similar way for the magnetostrictions cannot give a satisfactory agreement with all the nine observed effects, except for the qualitative H^2 dependence. A more realistic model is needed; in particular, the nonscalar nature of the field, which is of primary importance in this anisotropic system, must be introduced with care in the free energy, while in the scaling model used here it plays a more or less isotropic role as does the temperature.

IV. CONCLUSION

CeNi is the intermediate-valence compound in which the charge and spin fluctuations give rise to the strongest and most anisotropic effects on thermal expansion and magnetostriction. Whereas the scaling-law model of Takke *et al.*[1] gives a rather good account of the volume effects, it fails to describe the observed anisotropic effects. The strong anisotropy, especially the unusual behavior along $\hat{b}$, may be associated with the covalent character of the 4f-5d-3d hybridization which is responsible for the intermediate-valence state.

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