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Thermal expansion of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ at ambient and high pressures

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$\text{Ce}_3\text{Bi}_4\text{Pt}_3$ is a cerium compound that exhibits a hybridization gap and concomitant semiconducting behavior in the coherent ground state. Using neutron powder diffraction, we have determined the variation of the lattice constant with temperature at two pressures ($P = 10^{-3}$ and 17.7 kbar), and determined the bulk modulus and atomic mean-square displacements for $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and its normal analog, $\text{La}_3\text{Bi}_4\text{Pt}_3$. The thermal expansion $\Delta\beta$ in $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ exhibits a maximum at $T_{\text{max}} = 50$ K at ambient pressure. Below 50 K, the bulk modulus ΔB is proportional to $T\Delta\beta$. We apply a Grüneisen analysis, under the assumption that the free energy exhibits $T/T_0(V)$ scaling. The Grüneisen parameter deduced from the ratio $\Delta B/T\Delta\beta$ is consistent with the value $\Omega = 36$ deduced from the pressure variation of T_{max} . The analysis allows us to predict the temperature dependence of the $4f$ specific heat ($\Delta C \propto \Delta\beta/\Omega$), which thus has a maximum at 50 K and a high-temperature entropy nearly equal the expected value $R \ln 6$. We argue that the maximum at 50 K reflects an (indirect) hybridization gap of order 100 K. We show further that the lattice constant anomaly Δa_0 is proportional to the effective moment $T\chi$; this suggests that a relationship known to be valid for antiferromagnets, namely $\partial(T\chi)/\partial T \propto \Delta C$ where ΔC is the specific heat, may be valid for $\text{Ce}_3\text{Bi}_4\text{Pt}_3$. Finally, we show that the temperature dependence of the mean-square atomic displacements is nearly identical for $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and $\text{La}_3\text{Bi}_4\text{Pt}_3$ and can be fitted by a simple Debye-Waller model; hence the expansion anomaly does not affect the average lattice dynamics.

INTRODUCTION

Thermal-expansion anomalies are widely observed in metallic Ce, Eu, Yb, and U compounds.¹ These are often discussed² via a thermodynamic ("Grüneisen") analysis, which depends on the assumption that the free energy exhibits characteristic energy scaling: $F(T, V) = NkTf[T/T_0(V)]$. The volume dependence is then characterized by an electronic Grüneisen parameter $\Omega = -\partial \ln T_0 / \partial \ln V$, which varies from 10 to 20 for mixed-valence compounds where $T_0 \approx 100$ –500 K, to much larger values (50–150) for heavy-fermion compounds with $T_0 \approx 10$ K. The scaling law leads to relations between the thermal expansion, specific heat, and compressibility that have been experimentally observed in a variety of Ce, Yb, and U intermetallic compounds.^{2,3}

Less attention has been given to the thermal expansion in compounds such as YbB_{12} , which have nonmetallic ground states,⁴ i.e., millivolt-gap semiconducting behavior. Recently, we reported⁵ the magnetic and transport properties of a new compound, $\text{Ce}_3\text{Bi}_4\text{Pt}_3$. For modestly high temperatures its properties are indistinguishable from those of metallic cerium compounds that are weakly mixed valence ($z \approx 3.1$ and $\eta_f \approx 0.9$) and that have characteristic (single-ion Kondo) temperatures T_K in the range of a few hundred degrees Kelvin. For example, the susceptibility⁵ shows a broad maximum near $T\chi = 80$ K

with Curie-Weiss behavior at higher temperatures; the resistivity is large ($\approx 200 \mu\Omega \text{ cm}$ at 300 K) and has $d\rho/dT < 0$; the inelastic neutron line shape above 100 K is broad and relatively featureless with a half-width $h\omega_0 = 20$ meV.⁶ Preliminary measurements⁷ of the L_{III} -edge x-ray absorption suggest $n_f \approx 0.9$. Such high-temperature behavior also follows the predictions of the single-impurity Anderson model for the nearly-integral-valence ($n_f \approx 1$) case. The Kondo effect in the model causes $d\rho/dT$ to be negative and the relationship $3kT\chi \approx \hbar\omega_0 \approx kT_K$ (implying $T_K \approx 240$ K for $\text{Ce}_3\text{Bi}_4\text{Pt}_3$) follows from $1/N$ expansion or Bethe-ansatz solutions.^{8,9}

However, at low temperatures the transport behavior (resistivity, Hall coefficient, and thermopower)^{5,10} is consistent with the presence of a gap in the electronic excitation spectrum with an activation energy of order 50 K; the specific heat below 20 K fails to show the large electronic contribution observed in metallic heavy-fermion compounds; and the neutron inelastic scattering is suppressed to zero below 12 meV.⁶ This behavior is similar to that of YbB_{12} (Ref. 5) and suggests a similar interpretation—that $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ is a small-gap semiconductor. Such behavior is also consistent with the "standard model" for Ce compounds: single-impurity Anderson-model behavior is expected at high temperatures, whereas the correlations and/or interactions responsible for the coherent ground state, whether metallic

or semiconducting, set in at temperatures well below T_K .

In this paper we report measurements of the temperature dependence of the lattice constant of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and its normal analog, $\text{La}_3\text{Bi}_4\text{Pt}_3$, at two pressures (10^{-3} and 17.7 kbar). We use these data to determine the volume-expansion coefficient and to give an estimate of the bulk modulus. We determine the Grüneisen parameter ($\Omega \approx 36$) and show that the low-temperature bulk modulus and thermal expansion are related as predicted for a system exhibiting characteristic energy scaling. The analysis allows us to predict the temperature dependence of the $4f$ contribution to the specific heat, which is difficult to measure in the given temperature range (20–300 K); the predicted specific heat is reasonable in that it gives the expected high-temperature entropy ($R \ln 6$). We relate these results to transport, susceptibility, and inelastic-neutron-scattering results using recent theoretical results¹¹ for the Anderson lattice; this allows us to give a sensible estimate of the indirect hybridization gap.

We then show that the lattice-constant anomaly Δa_0 is proportional to the “effective moment” $T\chi$ and argue that this may follow from a relationship $\partial(T\chi)/\partial T \propto \Delta C$ known to be valid for antiferromagnets. Finally, we discuss the observation that the temperature dependence of the local mean-square displacements for the constituents of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ shows no anomalies, suggesting that the volume-expansion anomaly does not affect the average lattice dynamics.

EXPERIMENTAL DETAILS

The $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and $\text{La}_3\text{Bi}_4\text{Pt}_3$ samples consisted of ground small single crystals grown in an excess bismuth flux. Neutron-diffraction data at ambient pressure for each sample were collected over a series of temperatures using $\pm 148^\circ$ and $\pm 90^\circ$ detector banks of the Neutron Powder Diffractometer at the Manuel Lujan, Jr. Neutron Scattering Center (LANSCE) at Los Alamos National Laboratory. The diffractometer constants were calibrated to the lattice constant of CaF_2 [5.463 85(2) Å at 302 K], which was in turn obtained from x-ray powder-diffraction measurements using the Cu $K\alpha$ radiation wavelengths given by Deslattes and Henins,¹² and the incident spectrum was measured using the scattering from a vanadium rod. Samples were cooled with an Applied Physics Laboratory helium refrigerator and the temperature was controlled with a Lake Shore Cryogenics DRC-93 temperature controller. Structural models corresponding to the cubic ($I\bar{4}3d$), structures for $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ or $\text{La}_3\text{Bi}_4\text{Pt}_3$ and a small amount of bismuth impurity were refined using the Generalized Structure Analysis System Rietveld code.¹³ Such use of Rietveld-profile analysis of time-of-flight neutron-diffraction data obtained at a spallation source, using data over the large d -spacing range of 0.4–6.6 Å, allows for a very precise determination of the lattice constants, and simultaneously allow determination of the site-specific Debye-Waller factors.¹⁴ Lattice constants at 17.7 kbar were collected with the $\pm 90^\circ$ detector banks of the lower-resolution High Intensity Powder Diffractometer at LANSCE. The samples, with a small

amount of NaCl pressure calibrant and Fluorinert pressure medium, were loaded into a Cu-Be self-clamping pressure cell. This cell, like the ambient-pressure vanadium sample tubes, was also mounted on the helium refrigerator. A boron nitride collimator was used to reduce the number of neutrons detected that were not scattered by the sample. The diffractometer constants were again obtained from CaF_2 calibrations and the incident spectrum was measured from a vanadium rod placed in the pressure cell. Lattice constants were obtained from Rietveld refinement, this time with three phases present: the $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ or $\text{La}_3\text{Bi}_4\text{Pt}_3$, the NaCl pressure calibrant, and a small amount of tungsten carbide from the piston that was not blocked by the collimator (neither of these samples appeared to contain any bismuth flux). The pressure was obtained from the lattice constant of NaCl using the equation of state given by Skelton *et al.*¹⁵

RESULTS AND ANALYSIS

The results of the Rietveld fits to the lattice constants and isotropic Debye-Waller factors for $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and $\text{La}_3\text{Bi}_4\text{Pt}_3$ are given in Figs. 1 and 2. [For ambient-pressure experiments, the coordinate x for Bi atoms on the $16e$ site was found to vary smoothly from $x=0.0857$ at $T=15$ K to 0.0853 at room temperature; however, for the high-pressure experiments, the atomic positions were set to an average value (0.0856 Å) and not refined further.] For the ambient-pressure data, the good quality of the fits is attested to by the low values of $\langle \chi^2 \rangle$ for the refinements, which were typically 1.5–2.0. The weighted-profile agreement factors R_{WP} and the expected agreement factor $R_{\text{exp}} = R_{\text{WP}} / \langle \chi^2 \rangle^{1/2}$ were generally

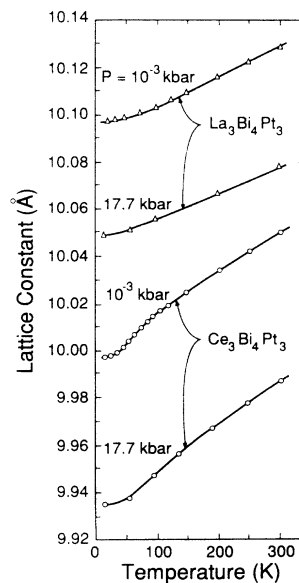


FIG. 1. The lattice constant a_0 for $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and $\text{La}_3\text{Bi}_4\text{Pt}_3$ as a function of temperature at $P=10^{-3}$ and 17.7 kbar. Typical errors representing one standard deviation for the refined lattice constants are 3×10^{-5} Å at ambient pressure and 5×10^{-5} Å at 17.7 kbar.

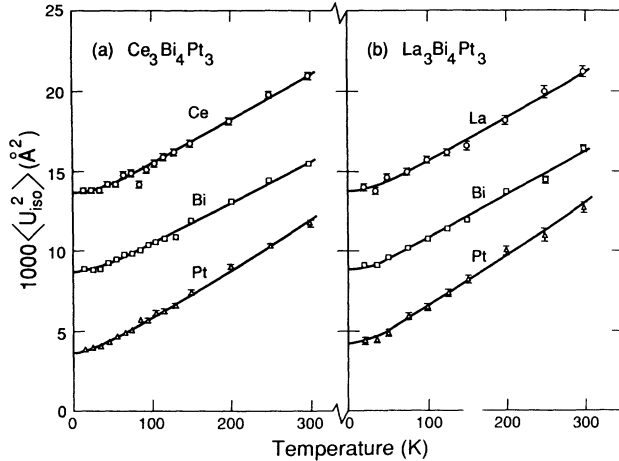


FIG. 2. The isotropic thermal parameters (mean-square atomic displacements) vs temperature for (a) $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and (b) $\text{La}_3\text{Bi}_4\text{Pt}_3$ at $P=10^{-3}$ kbar. The curves are fits to a two-term Debye-Waller model (Ref. 14). In each panel, the curves for Bi and Ce/La are displaced upwards by 5 and 10\AA^2 , respectively. Error bars representing one standard deviation in the refined thermal parameters are omitted where they are smaller than the size of the symbols.

around 14% and 10%, respectively, which are typical for high-resolution neutron data with low backgrounds. For the 17.7-kbar data, the values of $\langle \chi^2 \rangle$ were typically 3.0, and the weighted-profile agreement factors R_{WP} and the expected agreement factor R_{expec} were 15% and 10%, respectively. These latter values are high for the lower-resolution neutron data and reflect the difficulty of carrying out experiments with samples in Cu-Be high-pressure cells.

From Fig. 1 it can be seen by comparison to $\text{La}_3\text{Bi}_4\text{Pt}_3$ (in which La is trivalent and metallic) that the thermal expansion of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ is anomalously large in the range 0–200 K. To quantify this, we plot in Fig. 3 the volume-expansion coefficient $\beta = (1/V)dV/dT = (3/a_0)da_0/dT$ for both compounds, and the difference $\Delta\beta$, which represents the $4f$ contribution to the thermal expansion. This peaks at $T_{\text{max}} = 50$ K at a value of $6.6 \times 10^{-5} \text{ K}^{-1}$ for $P = 10^{-3}$ kbar and near 85 K at a value of $5.5 \times 10^{-5} \text{ K}^{-1}$ for $P = 17.7$ kbar.

An estimate of the isothermal bulk modulus can be obtained by interpolating between the $a_0(T)$ curves for the two different pressures and evaluating $B \approx -(a_0/3)(\Delta P/\Delta a_0)$. This procedure will be in error to the extent that $V(P)$ is nonlinear (nonlinearity may occur in the range where V varies rapidly with temperature). The bulk modulus so determined is shown in Fig. 4.

If the free energy obeys a scaling law

$$F = F_0(T, V) + \Delta F(T, V), \quad (1a)$$

$$\Delta F(T, V) = NkTf[T/T_0(V)], \quad (1b)$$

then it is straightforward to show^{2,3} that

$$\Delta\beta = \Omega\Delta C/VB, \quad (2)$$

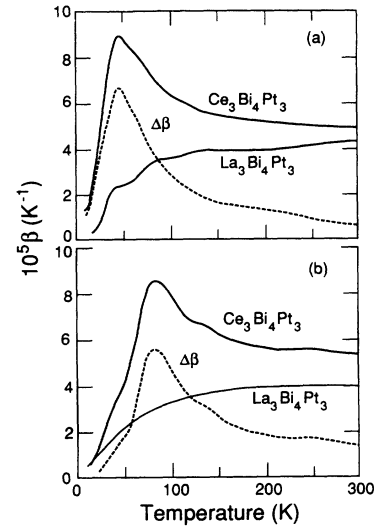


FIG. 3. The volume-expansion coefficients β for $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and $\text{La}_3\text{Bi}_4\text{Pt}_3$ at (a) $P = 10^{-3}$ and (b) 17.7 kbar obtained from the data shown in Fig. 1 by fitting cubic splines and then differentiating. $\Delta\beta$ is the difference between the two curves and represents the effect of the $4f$ electron. According to the Grüneisen analysis, this should be proportional to the specific heat with a proportionality constant 1.27×10^5 J/mole Ce.

where $\beta = \beta_0 + \Delta\beta$, $C = C_0 + \Delta C$, and $B = B_0 + \Delta B$ are the volume-expansion coefficient, specific heat at constant volume, and bulk modulus, respectively, where the subscripted quantities are the background contributions (as estimated, for example, from $\text{La}_3\text{Bi}_4\text{Pt}_3$) and where $\Omega = -\partial \ln T_0 / \partial \ln V$ is the electronic Grüneisen parameter. Equation (2) depends only on the analyticity of f , which for the case at hand should be of activated form. At low temperatures $T \ll T_0$ the electronic contribution

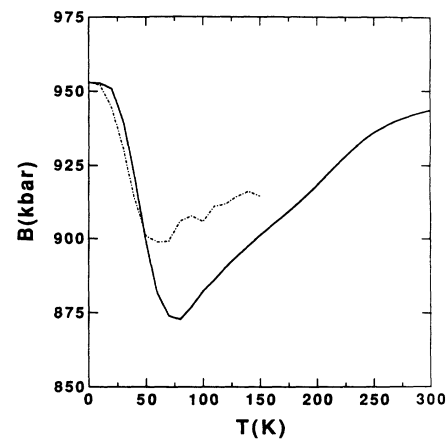


FIG. 4. Bulk modulus of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ obtained from spline fits to the data of Fig. 1 by the linear approximation $B = -(a_0/3)\Delta P/\Delta a_0$. The dashed line represents ΔB_G , the prediction of the Grüneisen analysis for the anomaly in the bulk modulus using the data from Fig. 3 and a Grüneisen constant $\Omega = 36$, with $\Omega^{(2)} = \Omega^2$ (see text).

to the bulk modulus can be written

$$\Delta B \cong -BT\Omega_{\text{eff}}\Delta\beta, \quad (3)$$

where

$$\Omega_{\text{eff}} = \Omega[1 - 1/2(\Omega^{(2)}/\Omega^2)] \quad (4)$$

and

$$\Omega^{(2)} = (V^2 T_0)(\partial^2 T_0 / \partial V^2). \quad (5)$$

[The correction to Eq. (3) is an order higher in T/T_0 .] Determination of ΔB and $\Delta\beta$ thus allows determination of $\Omega^{(2)}$ if Ω is already known. While $\Omega^{(2)}$ is often neglected,² this is not advisable, as can be seen from the plausible case $T_0 \propto V^{-\Omega}$, where $\Omega^{(2)} = \Omega^2$ and $\Omega_{\text{eff}} = \frac{1}{2}\Omega$.

To estimate Ω we assume T_0 is proportional to the temperature T_{max} where $\Delta\beta$ is maximum. [According to Eq. (2), this is also the temperature where ΔC is maximum; in theoretical treatments^{8,9,11} this varies proportionally with the characteristic energy.] We then have $\Omega = B\Delta T_0 / (T_0 \Delta P) = 36$. In Fig. 4 we compare the quantity $\Delta B_G = -BT\Omega_{\text{eff}}\Delta\beta$ to the measured ΔB . A value $\Omega_{\text{eff}} = 18$ was utilized, which implies $\Omega^{(2)} = \Omega^2$. We note that ΔB_G fits the data fairly well for $T < 50$ K; presumably for higher temperatures the above-mentioned correction to Eq. (3) needs to be included.

Although the specific heat has not been measured above 20 K, we can nevertheless use Eq. (2) to estimate it, i.e., $\Delta C = V\Delta\beta / (\partial \ln T_0 / \partial P)$. For $V = 1000 \text{ \AA}^3$ per 12 Ce atoms in the unit cell and $\partial \ln T_0 / \partial P = 0.04$ kbar, this gives $\Delta C = (1.27 \times 10^5 \text{ J/mol Ce})\Delta\beta$. The dashed line in Fig. 3, when multiplied by this factor, in our estimate of the specific heat. The estimated entropy, obtained by integrating the estimated specific heat, is shown in Fig. 5. We note that the saturation entropy (12.7 J/mole Ce K) is close (within our 15% determination of Ω) to the value $R \ln 6$ expected for Ce ($J = \frac{5}{2}$).

The anomalous contribution $\Delta a_0(T)$ to the lattice con-

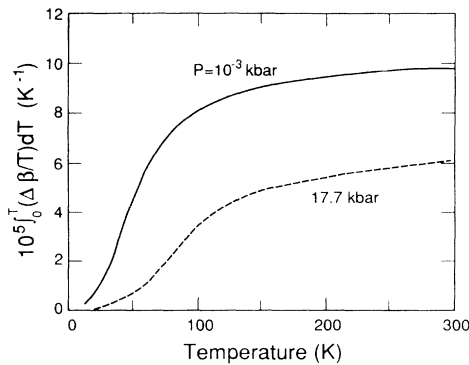


FIG. 5. The integral $\int_0^T (\Delta\beta/T) dT$ plotted as a function of temperature at $P = 10^{-3}$ and 17.7 kbar. Given the assumptions discussed in the text, this should be proportional to the entropy, with a proportionality constant of order 1.27×10^5 J/mol Ce. The entropy saturates to a value comparable to the value $R \ln 6$ expected for a $J = \frac{5}{2}$ multiplet.

stants of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ can be defined via

$$a_0(T) = a_{\text{normal}}(T) + \Delta a_0(T), \quad (6)$$

where $a_{\text{normal}} = a_0(T=0) + [a_{0,\text{La}}(T) - a_{0,\text{La}}(T=0)]$; i.e., we subtract the normal thermal expansion as estimated from the data for $\text{La}_3\text{Bi}_4\text{Pt}_3$. In Fig. 6 we show that above 20 K Δa_0 is proportional to the “effective moment” $T\chi$ where χ is the magnetic susceptibility. This proportionality will be discussed further below.

DISCUSSION

The Grüneisen analysis correctly predicts the proportionality between the measured bulk modulus and thermal expansion below 50 K and allows us to predict the temperature dependence of the specific heat, with a reasonable prediction for the high-temperature entropy ($R \ln 6$). This strongly supports the scaling assumption $F(T, V) = NkTf[T/T_0(V)]$, at least at low temperatures. The widely accepted microscopic theory for cerium compounds, the single-impurity Anderson model, exhibits T/T_K scaling in the nearly-integral-valence ($n_f \approx 1$) Kondo regime.^{8,9} This provides a natural basis for understanding the Grüneisen analysis. However, for $\text{Ce}_3\text{Bi}_4\text{Pt}_3$, the temperature of the thermal-expansion anomaly (50 K) is comparable to the activation energy deduced from transport measurements; this suggests that the thermal-expansion peak is not a single-ion effect, but rather that it arises from the excitation of 4*f* electrons when the temperature becomes comparable to the gap Δ . The relevant theory, that of the Anderson lattice, is still poorly understood. A general feature of most work^{11,16} is the existence of a “hybridization gap” at $T = 0$ K whose width is comparable to the single-ion Kondo temperature. This gap renormalizes (vanishes) as the temperature is raised. The general expectation is that T/T_K scaling should still be valid.

A recent mean-field slave-boson treatment⁽¹¹⁾ of the Anderson lattice predicts an indirect gap Δ_{ind} for excitations from the zone center to the zone boundary with magnitude proportional to $(1 - n_f)V^2\rho$, where $n_f(T)$ is the 4*f* occupation number, V the 4*f*-conduction hybridization matrix element, and ρ the background density of states. For a certain range of parameters, the theory predicts maxima in $\chi(T)$ and $\Delta C(T)$ at temperatures of order $\Delta_{\text{ind}}/2k_B$ and a threshold in the $T = 0$ inelastic scattering cross section $\chi''(\omega)$ at $\omega = \Delta_{\text{ind}}$ for $Q = 2\pi/a_0$.

Our analysis predicts $T_{\text{max}} = 50$ K for the specific heat; other data⁵ show $T_{\text{max}} = 80$ K for the susceptibility. Neutron-scattering data for polycrystalline $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ shows⁶ a threshold near 12 meV. Hence this body of data gives and estimate for the indirect gap of 100–160 K.

The value of the Grüneisen parameter $\Omega = 36$, is comparable to the value expected for *metallic* heavy-fermion compounds with comparable T_K . Indeed, in the reported temperature range the thermal-expansion anomaly is very similar in shape and magnitude to anomalies reported in metallic systems such as CeSn_3 .² To distinguish $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ from the metallic case would require more pre-

cise measurements at lower temperatures, where the thermodynamics should be of activated form.

The proportionality demonstrated in Fig. 6 between the lattice-constant anomaly Δa_0 and the effective moment $T\chi$ leads to the relation

$$T\chi \propto (3/a_0)\Delta a_0(T) = \int_0^T (3/a_0)(\partial a_0/\partial T)dT. \quad (7)$$

(The a_0 in the denominator is constant to 0.5% over the whole temperature range and can thus be treated as a constant.) The integrand is $\Delta\beta(T)$, which, through the Grüneisen analysis, is proportional to $\Delta C(T)$. It then follows that $\partial(T\chi)/\partial T \propto \Delta C$. A similar relationship was shown by Fisher¹⁷ to be valid for antiferromagnets in the vicinity of the Néel temperature. It is not clear to us why it should hold for $\text{Ce}_3\text{Bi}_4\text{Pt}_3$. It certainly is not a property of the theory. Analysis of the predictions of Ref. 11 suggests that $T\chi$ is proportional to the entropy for a Kondo insulator; this is also expected for heavy-fermion metals where $\Delta C = \gamma T$ and $T\chi \cong T\chi(0) \propto \gamma T$.

Finally, we turn to the isotropic thermal parameters U_{iso}^2 , which are plotted in Fig. 2 for each site in each compound. Since the site symmetries (4, 3, and 4 for the Ce/La, Bi, and Pt sites, respectively), are not cubic, the U_{iso}^2 are orientational averages [in fact, use of an anisotropic model for the thermal parameters for $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ at 300 K gave values for thermal ellipsoid major to minor-axis ratios that range from 1.47(12) for Pt to 1.26(8) for Bi]. The solid lines represent fits using a Debye-Waller model for the temperature dependence of the mean-square atomic displacements; this allows extraction of Debye-Waller temperatures for each site¹⁴ (Table I). If we mass-weight these temperatures, we obtain averaged Debye temperatures $\Theta_D \approx 167$ and 164 K for $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and $\text{La}_3\text{Bi}_4\text{Pt}_3$, respectively. These values compare quite favorably to the estimates of 200 and 175 K, respectively, obtained from the low-temperature specific heat.^{5,10} Examination of Table I shows that although the Debye-Waller temperatures on the Pt and Bi sites increase slightly on going from $\text{La}_3\text{Bi}_4\text{Pt}_3$ to $\text{Ce}_3\text{Bi}_4\text{Pt}_3$, the rare-earth Debye-Waller temperatures remains essentially the same. Since the mean-square displacements represent an

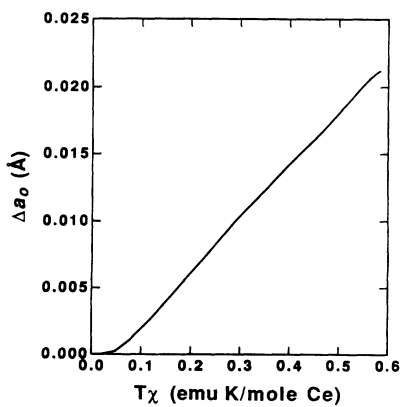


FIG. 6. The lattice constant anomaly Δa_0 (see text) plotted against the “effective moment” $T\chi$ with temperature as an implicit variable. The data for the susceptibility are from Ref. 5.

TABLE I. Atomic Debye-Waller temperatures for the constituents of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and $\text{La}_3\text{Bi}_4\text{Pt}_3$ at ambient pressure obtained by fitting the temperature dependence of the isotropic thermal parameters to a two-term Debye-Waller model (Ref. 14). Numbers in parentheses denote one standard deviation in the last digit(s) of the refined parameters.

Compound or atom	Debye temperature (K)
$\text{Ce}_3\text{Bi}_4\text{Pt}_3$	
Ce	190(2)
Bi	163(1)
Pt	155(1)
$\text{La}_3\text{Bi}_4\text{Pt}_3$	
La	191(2)
Bi	158(1)
Pt	150(2)

average of the phonons over the whole zone, these results imply that the thermal-expansion anomaly is not accompanied by a change in the average phonon displacements. This is not unexpected; very little overall softening of phonons is observed in compounds such as CeSn_3 and CePd_3 .¹ The softening of the bulk modulus apparently affects phonon modes in only a small fraction of the Brillouin zone.

CONCLUSIONS

The ground state of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ is that of a small-gap semiconductor. Measurements of the thermal expansion in $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and the nonmagnetic analogue $\text{La}_3\text{Bi}_4\text{Pt}_3$ at ambient pressure reveal an f -derived anomaly $\Delta\beta$ near 50 K that is shifted to higher temperature with applied pressure. From these measurements, we find a temperature-dependent bulk modulus that varies as $T\Delta\beta$ below 50 K, in agreement with a Grüneisen analysis that assumes the f -derived free energy scales with a volume-dependent characteristic temperature. The deduced electronic Grüneisen parameter $\Omega = 36$ and the overall behavior of $\Delta\beta(T)$ for 20–300 K is similar to the behavior of moderately heavy-fermion compounds such as CeSn_3 , which have a characteristic temperature scale of the order of room temperature. The Grüneisen analysis implies that the specific heat peaks at 50 K; recent theory suggests that this results from a direct gap in the excitation spectrum of order 100 K. This is consistent with estimates (140–160 K) derived from neutron scattering or the susceptibility. We also find a linear relationship between the “effective” moment $T\chi$ and the f contribution to the lattice-parameter change with temperature. Although such a relationship is expected to hold near an antiferromagnetic phase transition, we believe this is the first time such a correlation has been noted over such a large temperature interval in a nonordering system.

Since the proportionality between ΔB and $\Delta\beta$ is only expected to be valid at very low temperature, while the proportionality between ΔC and $\Delta\beta$ should be valid over the whole temperature range, a key experiment to test the Grüneisen assumption ($F(T, V) = NkTf[T/T_0(V)]$) is to measure the specific heat directly over the range 0–300

K. Furthermore, since the low-temperature specific heat is expected to be activated, a more precise determination of thermal expansion and bulk modulus (e.g., by ultrasonic experiments) at low temperatures would allow for a more stringent test of the Grüneisen analysis at temperatures where the small-gap semiconducting behavior is distinctly different from metallic heavy-fermion behavior.

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