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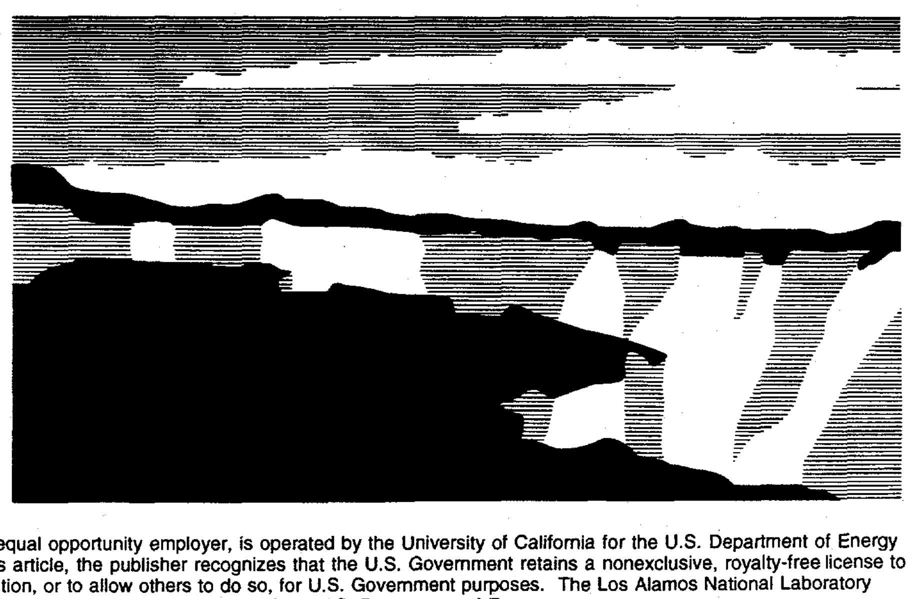

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MAGNETOSTRICTION AND THERMAL EXPANSION OF THE KONDO SEMICONDUCTOR $Ce_3Bi_4Pt_3$

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ABSTRACT

We report dilatometric thermal expansion (α) and magnetostriction (λ) measurements on the Kondo semiconductor $Ce_3Bi_4Pt_3$ and its non-magnetic analog $La_3Bi_4Pt_3$ in fields to 100 kOe. The magnetic contribution to the thermal expansion of $Ce_3Bi_4Pt_3$ displays a broad maximum centered at 50 K, close to the temperature where the 4*f* specific heat is a maximum. The linear magnetostriction is anomalously large in $Ce_3Bi_4Pt_3$, with values that are characteristic of mixed-valent compounds ($\lambda_\perp = 3.26\times10^{-5}$, $\lambda_\parallel = -6.24\times10^{-5}$ in 100 kOe at 4 K). The volume magnetostriction is positive and a factor of ten smaller than the linear coefficients ($\lambda_V = 2.75\times10^{-6}$ in 100 kOe at 4 K). The volume magnetostriction is temperature-dependent, and peaks at 50 K. The data are considered in terms of a Grüneisen analysis that links the temperature-dependent magnetic susceptibility, thermal expansion, magnetostriction, bulk modulus, and specific heat of $Ce_3Bi_4Pt_3$ via temperature-dependent electronic and magnetic scaling parameters.

1. Introduction

A key feature of rare-earth mixed-valent (MV) systems is that there is a clear correlation between the f-ion's atomic volume and its valence state.[1] In MV Ce compounds, for example, the valence state is a mixture of the Ce^{4+} (J = 0) state and the (spatially smaller) Ce^{3+} (J = 5/2) state. The valence state in these materials is typically temperature-dependent due to many-body renormalization.[2] The overall valence is also field-dependent because the resulting Zeeman energy favors the magnetic ($J \neq 0$) configuration; hence, an applied H-field will make a MV Ce compound more trivalent.[3] As

a result, MV systems commonly display thermal expansion and volume magnetostriction effects that are anomalously large.[2]

We consider here the thermal expansion (α) and magnetostriction (λ) of the Kondo semiconductor $Ce_3Bi_4Pt_3$. $Ce_3Bi_4Pt_3$ is a mixed-valent ($T_K \approx 300$ K) narrow-gap semiconductor[4] wherein the energy gap stems from band hybridization between a conventional conduction band and a renormalized f band; there is strong experimental evidence that the renormalization is driven by Kondo-like many-body correlations.[4-6] Dilatometry measurements indicate that this material's α and λ are quite large and are entirely characteristic of a MV compound. The electronic (Ω_e) and magnetic (Ω_H) Grüneisen parameters extracted from the data via thermodynamic scaling arguments[1,7] are also consistent with mixed-valent behavior.

2. Experimental Results

Single crystals of cubic $Ce_3Bi_4Pt_3$ and its non-magnetic analog $La_3Bi_4Pt_3$ were grown with a Bi-flux technique.[4] The crystals form as 1 mm-thick rods that grown in the [111] direction. The polished samples employed in this work were 0.5 mm-thick along the dilatation direction. The thermal expansion $\alpha \equiv (1/L)(dL/dT)$ and magnetostriction $\lambda \equiv [L(H)-L(0)]/L(0)$ were measured in fields to 100 kOe and in the temperature range 4–200 K with a compact dilatometer.[8] Both the parallel ($\lambda_{\parallel}$) and perpendicular ($\lambda_{\perp}$) magnetostriction tensor components were measured by proper orientation of the cell. The magnetovolume effect $\lambda_V=\Delta V/V=\lambda_{\parallel}+2\lambda_{\perp}$ was determined from these measured quantities.

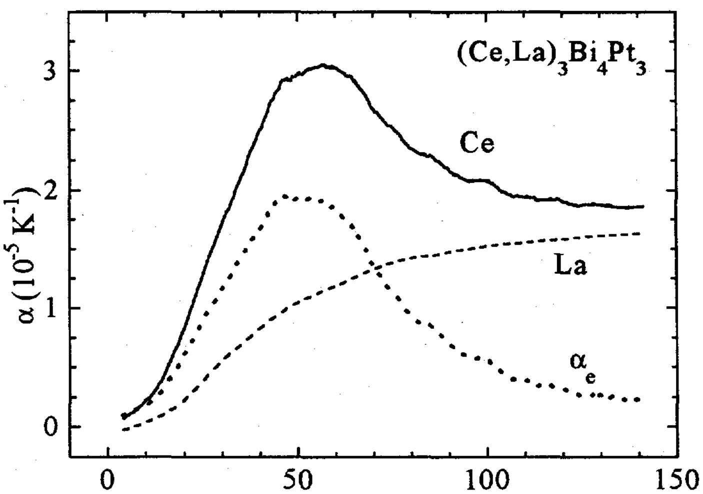

Fig. 1. Total thermal expansion of $Ce_3Bi_4Pt_3$ (solid line), $La_3Bi_4Pt_3$ (dashed line), and the 4*f* electronic contribution to the thermal expansion of $Ce_3Bi_4Pt_3$ (dotted line).

The thermal expansion of $Ce_3Bi_4Pt_3$ and $La_3Bi_4Pt_3$ are depicted in Fig. 1. The Ce compound exhibits an anomalous maximum in α near 55 K while the La analog's α is a monotonic function of temperature. The 4f electron contribution to the thermal expansion of $Ce_3Bi_4Pt_3$ can be separated from the lattice contribution by subtracting the La data from the Ce data. The resulting α_e is depicted in Fig. 1; this electronic contribution exhibits a broad peak centered near 50 K, quite close to the temperature were the 4f specific heat[9] C_e shows a similar broad maximum. These data are quantitatively similar to earlier thermal expansion results that employed power neutron diffraction measurements.[5]

The magnetostriction tensor of a cubic compound contains both diagonal ($\lambda_{||}$) and off-diagonal ($\lambda_{\perp}$) terms. The measured magnetostriction therefore depends on the direction that it is measured in (this is not the case for the thermal expansion because that tensor only has diagonal components) as well as upon the H-field direction. When the length change is measured along $\vec{a}$ with the field applied along $\vec{b}$, the measured magnetostriction is $\lambda_{\vec{a},\vec{b}} = \lambda_{ij} a_i^2 b_j^2$, where a_i and b_j are direction cosines and a summation over i and j is implied.[10] With cubic symmetry this expression simplifies to $\lambda_{\vec{a},\vec{b}} = \lambda_{||} a_i^2 b_i^2 + \lambda_{\perp}(1 - a_i^2 b_i^2)$. The single-crystal specimen used in this study was oriented along a $[3\bar{2}\bar{1}]$ direction as determined via Laue and x-ray diffraction measurements (growth morphology and sample size precluded the standard [100] orientation). The magnetostriction was measured along $[3\bar{2}\bar{1}]$ with the field oriented both parallel and perpendicular (along [111]) to this direction. The two measured values of λ are orthogonal linear combinations of the tensor components $\lambda_{||}$ and $\lambda_{\perp}$; these tensor components were determined algebraically from the raw data.

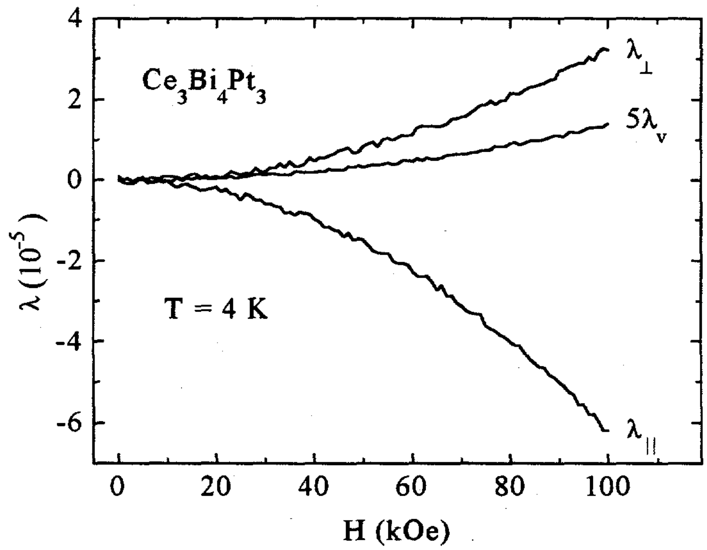

Fig. 2: linear and volume magnetostriction of $Ce_3Bi_4Pt_3$ at 4 K.

The linear and volume magnetostriction of $Ce_3Bi_4Pt_3$ at 4 K is depicted in Fig. 2. $\lambda_{||}$ and $\lambda_{\perp}$ are very large, are opposite in sign, and vary quadratically with field. The resulting volume effect is a factor of ten smaller than the linear coefficients and is positive. This indicates that, as with other MV Ce systems, the applied field favors the Ce^{3+} state. The magnitude of λ_V is comparable to that of other MV systems with T_K's of several hundred K ($CeSn_3$, $CePd_3$, and $CeBe_{13}$).[3] The temperature-dependent H^2 magnetostriction coefficients (S_V, $S_\parallel$, and $S_\perp$) are plotted in Fig. 3. The linear coefficients monotonically decrease with increasing temperature whereas the volume coefficient displays a broad maximum at 50 K; this is the same temperature where there is a peak in α_e and C_e. There was no detectable volume magnetostriction above 90 K.

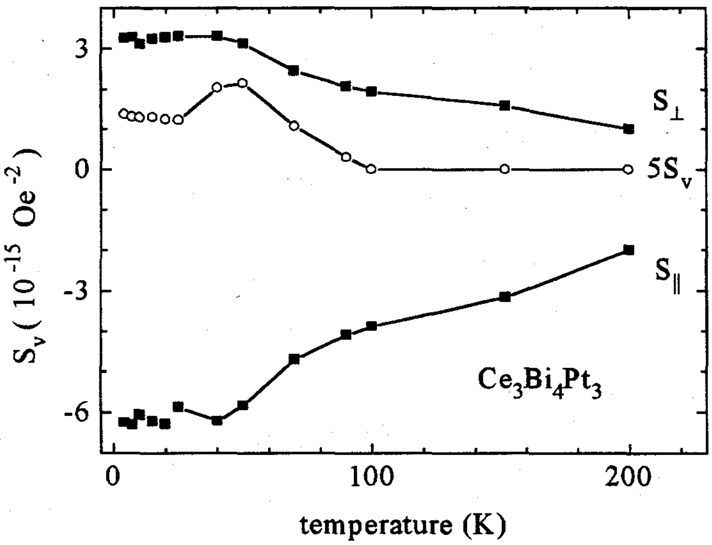

Fig. 3: Temperature-dependent H^2 coefficients for $\Delta V/V$ (S_V), $\lambda_\parallel$ ($S_\parallel$) , and $\lambda_\perp$ ($S_\perp$). Solid lines are guides to the eye.

3. Grüneisen Analysis

By utilizing a thermodynamic scaling approach, the thermal expansion, magnetostriction, specific heat, bulk modulus B, and magnetic susceptibility χ can be combined to determine the underlying Grüneisen parameters that characterize the thermodynamics of a mixed valent system. The electronic Grüneisen parameter is defined as $\Omega_e = -\partial lnT_o/\partial lnV$ while the magnetic Grüneisen parameter is defined as $\Omega_H = -\partial lnH_o/\partial lnV$, where T_o and H_o are the characteristic scaling temperature and magnetic field, respectively. If the magnetic and thermal degrees of freedom are fully coupled, there is a single energy scale ($\mu_B H_o = k_B T_o$) and $\Omega_e = \Omega_H$. When Maxwell's relation $\partial M/\partial P = -\partial V/\partial H$ is combined with the assumption that the mixed valent (4*f* electron) contribution to the free energy obeys the scaling law $F_e \propto -Nk_B T f(T/T_o, H/H_o)$, the aforementioned quantities are related by

$$C_e = \frac{3\alpha_e BV}{\Omega_e}, \qquad (1)$$

$$\text{and} \quad S_V = \frac{1}{2BV}\left[\chi[2\Omega_H - \Omega_e] + T\frac{\partial\chi}{\partial T}\Omega_e\right], \tag{2}$$

where $\lambda_V = S_V H^2$. With $\Omega_e = \Omega_H$, Eq. (2) simplifies to $S_V = (\Omega_e / 2BV)(\chi + T\partial\chi/\partial T)$. For $Ce_3Bi_4Pt_3$ the quantities α_e, C_e, S_V, and $T\partial\chi/\partial T$ all exhibit a broad maximum centered near 50–60 K (the bulk modulus is essentially T-independent).[5,9] Hence, these measured quantities exhibit the scaling behavior predicted by Eqs. (1) and (2).

By combining the measured data[5,9] with Eq. (1), $\Omega_e(T)$ can be determined; the results appear as open and closed squares in Fig. 4. The value at 50 K ($\Omega_e = 32$) agrees well with a previous Ω_e estimate based on the pressure dependence of the temperature where α_e is a maximum.[5]. Ω_e rapidly increases with decreasing temperature, and appears to saturate to a value of roughly 90 below 10 K. The same overall temperature dependence is observed in many other MV and heavy fermion systems.[1]

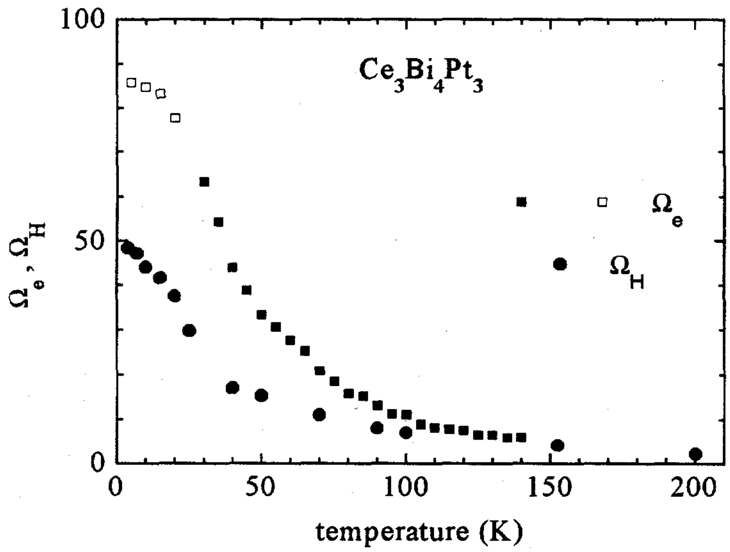

Fig. 4: Temperature-dependent electronic and magnetic Grüneisen parameters for $Ce_3Bi_4Pt_3$. Ω_e data at T < 25 K (open squares) were calculated by extrapolating C_e data (Ref. 9) to T=0.

When the magnetic Grüneisen parameter is set equal to Ω_e, S_V as predicted by Eq. (1) reproduces the overall temperature dependence exhibited by the data (Fig. 3) very well, but the amplitude is too high by a factor of 5. This suggests that the thermal and magnetic energy scales are decoupled in $Ce_3Bi_4Pt_3$. Therefore, Ω_H was calculated via Eq. (2) with the Ω_e values in Fig. 4; the results are presented in Fig. 4. $\Omega_H(T)$ is smaller then Ω_e, and it displays a temperature dependence that is similar to that of Ω_e. While the observation that $\Omega_H < \Omega_e$ could be an experimental artifact, it may reflect the theoretical strong-coupling prediction that the charge and spin energy gaps in a Kondo semiconductor should not be equivalent.[11]

In summary, the $4f$ thermal expansion, $4f$ specific heat, and volume magnetostriction of the Kondo semiconductor $Ce_3Bi_4Pt_3$ all display a peak near 50 K. These quantities, coupled with the magnetic susceptibility, obey a simple thermodynamic scaling law involving both a thermal and magnetic scaling parameter. As with other Ce MV compounds, the experimentally determined electronic and magnetic Grüneisen parameters are positive and display a characteristic temperature dependence which saturates at low temperatures.

4. Acknowledgments

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