Thermodynamics of FeSi

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We show that a simple model involving two narrow ($\simeq 500$ K) peaks in the density of states (DOS) at the edges of a narrow ($\simeq 1000$ K) gap can account for the observed anomalies in the magnetic susceptibility, specific heat, thermal expansion, and elastic response of FeSi. We also show that the resistivity of FeSi, including the metal-insulator "transition" at about 300 K, is well described by this model. Recent band-structure calculations, although predicting the correct value for the semiconducting gap, are unable to account for the narrow peaks in the DOS needed to explain the thermodynamics. We conclude that, given the available alternatives, a Kondo insulator description—involving an extreme renormalization of the noninteracting bands—is most appropriate for FeSi.

FeSi is a narrow-gap semiconductor that has long attracted the interest of solid-state physicists.[1–5] One of the most intriguing physical properties of FeSi is its magnetic susceptibility $\chi(T)$, which is small at low temperature but grows rapidly until it peaks near 500 K; above 500 K the susceptibility diminishes slowly, and can be described with a Curie-Weiss law. Not surprisingly, it was proposed[2] that the sharp drop in $\chi(T)$ was due to an antiferromagnetic transition, but neutron scattering,[3] Mössbauer,[4] and NMR (Ref. 4) measurements revealed no long-range magnetic order in FeSi.

An alternate explanation of $\chi(T)$ was proposed by Jaccarino *et al.*,[5] who considered two (quite similar) models. In the first model, two narrow bands equidistant from the chemical potential and separated by a gap of 1520 K were shown to explain the susceptibility, *but only in the limit of vanishing bandwidth.* In the second model, a two-level system with ground state $S=0$, excited state $S=\frac{1}{2}$, and a gap of 750 K was also shown to be compatible with the data. Because the authors found the zero-bandwidth requirement to be unphysical, they concluded that the second model, involving thermally excited *localized* spins, was probably correct.

Yet another explanation of $\chi(T)$ was offered by Takahashi and Moriya (TM),[6] who applied their spin-fluctuation theory of itinerant electron systems to FeSi. TM found that they could model $\chi(T)$ assuming FeSi is a band semiconductor with a small gap and a bandwidth of about 1 eV. In their model, the amplitude of local spin-density fluctuations increases strongly with temperature until saturation; at this point, the spin fluctuations can be regarded as a set of interacting local moments.[6] Subsequent neutron-scattering measurements by Shirane *et al.*[7] were interpreted as supporting the TM theory because the magnetic (band) electrons were found to be thermally excited.

Very recently, Mason *et al.*[8] observed that the spin-fluctuation spectrum of the Kondo insulator $Ce_xNi_{1-x}Sn$ was similar to that of FeSi. Based on this observation, the authors of Ref. 8 suggested that FeSi might represent the first example of a Kondo insulator involving the d electrons of a transition metal rather than the f electrons of a rare earth or actinide. Subsequent local-density-approximation band-structure calculations carried out by Mattheiss and Hamann[9] predicted an indirect semiconducting gap of $\simeq 0.11$ eV in FeSi, and bandwidths of $\simeq 0.5$ eV; the authors find that ordinary band theory cannot explain even qualitatively the temperature dependence of the susceptibility, but whether a spin fluctuation description or a Kondo insulator description is more appropriate they are unable to say. The inadequacy of band theory was also emphasized by Fu, Krijn, and Doniach,[10] who compared the optical conductivity $\sigma(\omega)$ predicted by band theory with the $\sigma(\omega)$ measured by Schlesinger *et al.*,[11] and found large discrepancies.

A distinguishing characteristic of Kondo insulators is an extreme renormalization of the noninteracting bands and bandwidths, which leads to a very large peak in the density of states (DOS) at the gap edges.[12–15] Such a pileup of states will produce anomalies in thermodynamic and transport properties which should be, to lowest order, describable in terms of a one-electron picture. In this paper we show that the temperature dependence of the magnetic susceptibility, specific heat, thermal expansion, elastic response, and resistivity can all be explained with a model DOS consisting of two narrow ($\simeq 500$ K) bands placed symmetrically about the chemical potential and separated by a small ($\simeq 1000$ K) semiconducting energy gap. Although not all of the above quantities can be fit with exactly the same parameters, the deviations are sufficiently small as to be explainable by sample-to-sample variation or by departures from simple one-electron behavior. We conclude that the existence of sharp peaks in the DOS at the gap edges—unexplainable in terms of conventional band theory—is strong evidence that a Kondo-insulator description of FeSi is appropriate.

The model we use is depicted schematically in the inset to Fig. 1: two rectangular bands, each of width W, are separated by an energy gap E_g. The number of electrons (and holes) in this model is given by $n_e=\int (Ng/W)f(E)dE$ where N is the number of unit cells, g is the number of states per unit cell, $f(E)$ is the Fermi function $f(E)=(\exp[(E-\mu)/k_BT]+1)^{-1}$, and the integration is over the conduction band. Due to the

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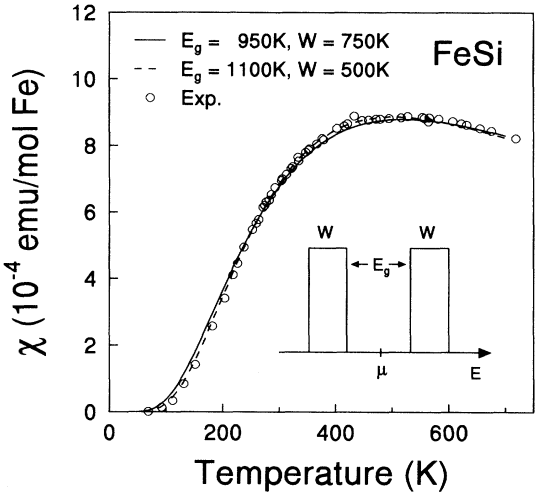

FIG. 1. Magnetic susceptibility of FeSi. Open circles: experimental points after Jaccarino *et al.* (Ref. 5). A low-temperature Curie tail was subtracted from the data as described in Ref. 5. Solid line: calculation using the model density of states shown in the inset with parameters $E_g=950$ K, $W=750$ K, and $g=4.40$ states/cell. Dashed line: calculation using parameters $E_g=1100$ K, $W=500$ K, and $g=4.20$ states/cell.

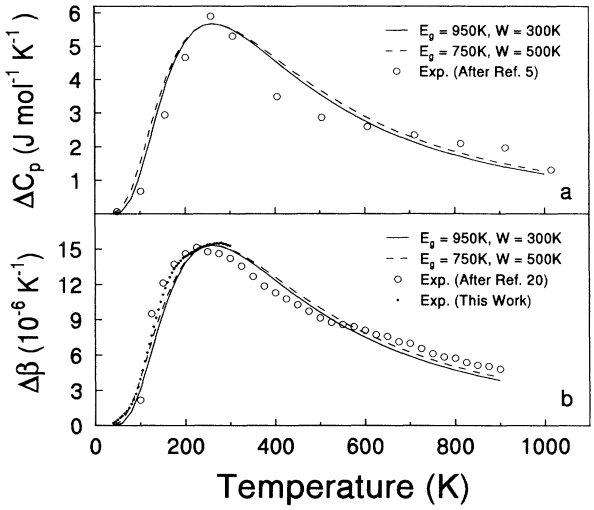

FIG. 2. (a) Open circles: anomalous electronic contribution to the specific heat of FeSi as estimated by Jaccarino *et al.* (Ref. 5) by taking the difference $[C_p(\mathrm{FeSi})-\gamma_{\mathrm{FeSi}}T]-[C_p(\mathrm{CoSi})-\gamma_{\mathrm{CoSi}}T]$, where γ is the Sommerfeld coefficient. As discussed in Ref. 5, the lattice contribution to the specific heat of CoSi should be similar to that of FeSi as these compounds are isostructural. Solid line: calculation using the model DOS described in the text with parameters $E_g=950$ K, $W=300$ K, and $g=0.80$ states/cell. Dashed line: calculation using $E_g=750$ K, $W=500$ K, and $g=0.84$ states/cell. (b) Open circles: estimate of the anomalous electronic contribution to the volume thermal expansion coefficient obtained by taking the difference $\beta(\mathrm{FeSi})-\beta(\mathrm{CoSi})$ of data from Ref. 20. Dots: $\beta(\mathrm{FeSi})-\beta(\mathrm{CoSi})$ obtained from capacitance dilatometry. The solid and dashed lines are calculations using the same parameters as used for the specific heat. The anomalous electronic contributions to the specific heat and thermal-expansion coefficient are related by a simple scale factor (see text).

particle-hole symmetry built into the model, the chemical potential μ resides in the center of the gap and is temperature independent. Physically, these rectangular bands represent peaks in the density of states at the gap edges, and should be thought of as riding upon a broad (semiconducting) background DOS.

The Pauli spin susceptibility of an electron system is given by

$$\chi(T)=-2\mu_B^2\int N(E)\frac{\partial f(E,\mu,T)}{\partial E}dE\ , \tag{1}$$

where $N(E)$ is the density of states (of one spin) and μ_B is the Bohr magneton. In Fig. 1 we show the magnetic-susceptibility data from Jaccarino *et al.*[5] and a calculation using Eq. (1) and the two sets of parameters indicated in the figure. Contrary to the claim in Ref. 5, in which it is stated that a satisfactory fit is obtained only in the limit $W\ll E_g/2$, we find that the susceptibility data can be modeled using a fairly wide range of parameters: 950 K $<E_g<1500$ K, and 0 K $<W<750$ K. In order to achieve acceptable fits, W must be made larger as E_g is reduced; the quantity (E_g+W) must be kept roughly constant.

In Fig. 2(a), we plot the anomalous electronic contribution to the heat capacity of FeSi as estimated by Jaccarino *et al.*[5] from the data of Ref. 16. Details of the estimate can be found in the figure caption. Also plotted in Fig. 2(a) is the contribution to the heat capacity arising from transitions across a narrow gap as calculated from our model DOS. This is obtained using $C_v=(\partial U/dT)_v$, with U given by

$$U=\int_{\text{valence band}}(Ng/W)Ef(E)dE+\int_{\text{conduction band}}(Ng/W)Ef(E)dE\ . \tag{2}$$

Again, the calculations were performed using two sets of parameters in order to give an indication of the acceptable range of these numbers.

If we compare the calculations of the susceptibility and the specific heat, we can find no single set of parameters that adequately models both. Specifically, if we consider the calculations in which $E_g=950$ K, we see that the bandwidths needed to fit the data ($W_\chi=750$ K and $W_{\Delta C_p}=300$ K) differ by more than a factor of 2. We attribute this difference to the extreme simplicity of our model, and to the fact that the susceptibility involves a derivative of the Fermi function, making it more sensitive to the detailed structure of the DOS. Also, it is likely that exchange and correlation effects are present, and these will affect the susceptibility differently than the specific heat.

It is interesting to compare the peak density of states

(of both spins) obtained from the calculations in which $E_g = 950$ K: $N(E)_\chi = 68$ states/eV cell, and $N(E)_{\Delta C_p} = 31$ states/eV cell. The difference is an indication that the susceptibility is enhanced with respect to that predicted by Eq. (1), and represents a breakdown of the one-electron approximation. As pointed out by Pines,[17] exchange and other effects that discriminate between the two electronic spin systems can lead to a larger value of the DOS inferred from measurements of the susceptibility than from the specific heat. Such Stoner-like enhancements of the susceptibility are common in metals,[18] and in transition metals like palladium, and transition-metal intermetallics like YCo_2, these enhancements can grow very large.

The relationship between the anomalous electronic contributions to the specific heat and the thermal-expansion coefficient is given by the Grüneisen relation[19]

$$\Delta\beta = \frac{\Omega_e(\Delta C_p)\chi_s}{V} , \tag{3}$$

where $\Delta\beta$ is the electronic contribution to the volume thermal-expansion coefficient, Ω_e is the electronic Grüneisen parameter, ΔC_p is the electronic contribution to the specific heat at constant pressure, χ_s is the background adiabatic compressibility, and V is the molar volume. If the anomalous contribution to the specific heat can be characterized by a single energy scale (such as a semiconducting energy gap), the electronic Grüneisen parameter gives the volume dependence of this energy and is expected to be roughly independent of temperature.

In Fig. 2(b), we plot the difference in volume expansion coefficients between FeSi and CoSi, which is an estimate of the anomalous electronic contribution to the thermal expansion of FeSi. The experimental data that extend to high temperature are from Ref. 20, and were obtained using a quartz dilatometer. The other experimental points were obtained by us using a capacitance dilatometer.[21] Also plotted in Fig. 2(b) are calculations using Eq. (3) and the same two sets of parameters used to fit the specific heat. The overall agreement is very good, indicating that a Grüneisen analysis is justified.

To calculate the electronic Grüneisen parameter, we use the value of the adiabatic compressibility obtained from low-temperature elastic modulus measurements[22] on FeSi, $\chi_s = 0.0054$ GPa^{-1}. We obtain $\Omega_e \simeq 7$ using Eq. (3) and either set of model parameters given in Fig. 2. It is significant that the magnitude of Ω_e for FeSi is comparable to the magnitude of Ω_e's found for mixed-valent metals such as $CeSn_3$ (Ref. 23) ($\Omega_e = 10$), and Kondo insulators such as SmB_6 (Ref. 24) ($\Omega_e = -11$). Such large Ω_e's are common in highly correlated systems, and indicate a strong volume dependence to the energy scale driving the thermodynamics.

The Helmholtz free energy of an electron system is given by $F = N\mu - k_B T \sum_k \ln(1+\exp[-E(E_k-\mu)/k_B T])$. Here N is the total number of particles and E_k is a one-particle energy. The coupling between Bloch electrons and elastic waves can be written $E_k = E_k^0 + d_{k\Gamma}\varepsilon_\Gamma$, where $d_{k\Gamma}$ is the deformation-potential coupling constant and ε_Γ is a symmetry strain. The effect of deformation-potential coupling on the elastic response can be calculated by first introducing the perturbed Bloch states into the expression for the free energy, and then taking the second derivative with respect to strain:[25]

$$c_\Gamma = \frac{\partial^2 F}{\partial \varepsilon_\Gamma^2} = c_\Gamma^0 - \frac{1}{k_B T}\sum_k \left[\frac{\partial E_k}{\partial \varepsilon_\Gamma}\right]^2 f_k(1-f_k) + \frac{1}{k_B T}\frac{\left[\sum_k \frac{\partial E_k}{\partial \varepsilon_\Gamma} f_k(1-f_k)\right]^2}{\sum_k f_k(1-f_k)} . \tag{4}$$

Here c_Γ^0 is the background elastic constant and f_k is the Fermi distribution function. For our simple two-band model, Eq. (4) simplifies to

$$c(T) = c^0(T) - (d_c - d_v)^2 \frac{1}{k_B T}\frac{Ng}{W}\left[\frac{I_v I_c}{I_v + I_c}\right] , \tag{5}$$

where d_v and d_c are the deformation-potential coupling constants for the valence and conduction bands, and I_v and I_c are defined by $I = \int f(1-f)dE$, with the range of integration extending over the valence (I_v) or conduction (I_c) band. In deriving Eq. (5), we have used a rigid-band approximation—i.e., we have assumed that the deformation potential coupling constants are independent of k within each band. It is important to note, however, that if $d_v = d_c$ then deformation coupling effects disappear.

In Fig. 3 we plot (open circles) the measured values of the elastic modulus c_{11} vs temperature for FeSi. These values were obtained dynamically using resonant ultrasound spectroscopy, a technique that is reviewed at length in Ref. 26. Also plotted in Fig. 3 (dashed line) is an estimate of the background c_{11}. This estimate was ob-

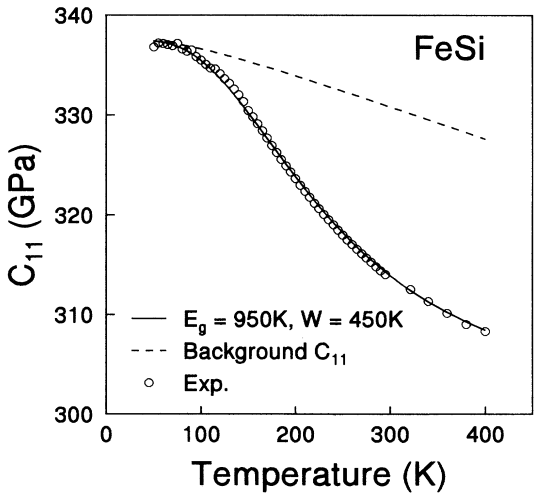

FIG. 3. Elastic modulus c_{11} vs temperature for FeSi. Open circles: experimental points. Dashed line: background c_{11} estimated from c_{11} (CoSi) as described in the text. Solid line: calculation using the model DOS described in the text with parameters $E_g = 950$ K, and $W = 450$ K.

tained from the c_{11} vs T data of Zinoveva, Andreeva, and Geld[27] on CoSi; the entire curve was displaced vertically by 2.5 GPa to achieve agreement at low temperature. Using our model density of states and Eq. (5), we were able to simulate (solid line) the temperature dependence of c_{11} using the parameters indicated in the figure.

Although we have shown that our model density of states can successfully explain the thermodynamics of FeSi, it still may be objected that an equally viable explanation may exist based on a picture of localized excitations (see, e.g., Ref. 5). To show that the same electrons participating in the thermodynamic anomalies also participate in the transport, we can calculate the temperature dependence of the resistivity using our model DOS. Recalling that $\rho \propto 1/n\mu$, where n is the carrier density and μ is the mobility, we can calculate $n(T)$ from our model DOS and then assume some reasonable temperature dependence for the mobility. An obvious starting point is to use $\mu(T) \propto T^{-3/2}$, as expected from electron-phonon scattering.[28] The calculation, together with the data, is shown in Fig. 4. Also shown in Fig. 4 is a calculation with wider bands and a slightly different temperature dependence to the mobility. The overall agreement is very good, especially at high temperatures. At lower temperatures we do not expect good agreement because conduction by ionized impurities begins to become important.

We can understand the overall behavior of the resistivity as follows. At high temperatures the resistivity is metallic because the carrier density is hardly changing (the narrow bands are approaching their infinite-temperature filling). As the temperature is lowered the temperature dependence of the carrier density begins to dominate, and the resistivity rises rapidly. At still lower temperatures ionized impurity conduction becomes important. The important point to note is that the combination of a small gap, narrow bands, and a reasonable temperature dependence to the mobility is sufficient to explain the resistivity of FeSi.

In summary, we have shown that a simple semiconductor model with two large peaks in the density of states at the gap edges can explain the thermodynamics and resistivity of FeSi. Ordinary band theory[9] predicts bandwidths that are roughly a factor of 10 too wide to explain the thermodynamics and resistivity. A Kondo insulator approach, however, seems to be compatible with the data. In Kondo insulator models[12–15] a flat band of f electrons (in FeSi these would be $3d$ electrons) hybridizes with a broad conduction band, with each unit cell containing an even number of electrons; the ground state is a narrow-gap semiconductor with extremely sharp peaks in the DOS at the gap edges. Although no comprehensive theory of a Kondo insulator exists at present, numerical

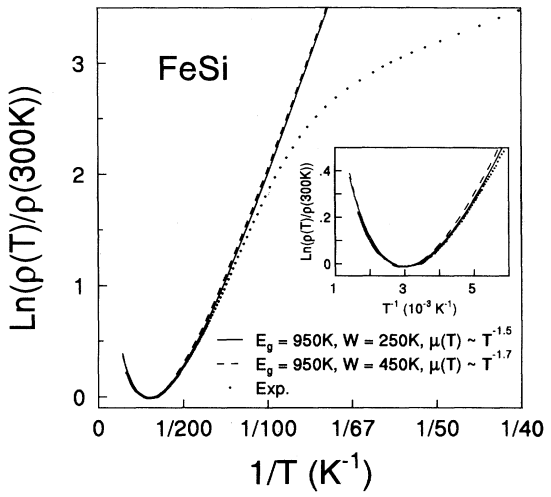

FIG. 4. Natural log of the normalized resistivity of FeSi vs temperature. Dots: experimental points. Solid line: calculation using the model DOS described in the text with the assumption that the mobility varies as $T^{-3/2}$. The parameters used were $E_g = 950$ K and $W = 250$ K. Dashed line: calculation with the same E_g and W used to fit c_{11} (see Fig. 3): $E_g = 950$ K and $W = 450$ K. The mobility varied as $T^{-1.7}$ in this calculation. Inset: Expanded view of the high-temperature portion of the figure.

calculations[12–14] indicate that the noninteracting bands are strongly renormalized, although the value of the gap remains roughly the same. We conclude that, among the existing alternatives, a Kondo insulator description is most consistent with the thermodynamics and resistivity of FeSi.

Note added in proof. Two recent papers that are directly relevant to the issues discussed here should also be mentioned; in Ref. 29, Sales and co-workers analyze the magnetic susceptibility and resistivity of FeSi using the same model DOS considered here, and arrive at quite similar conclusions. In Ref. 30, Park *et al.* report high-resolution angle-resolved photoemission experiments on FeSi that reveal a spectacularly sharp peak in the density of states at the gap edge. The observation of this peak strongly supports the phenomenological picture presented here.

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[1] G. Föex, J. Phys. Radium **9**, 37 (1938).
[2] R. Benoit, J. Chim. Phys. **52**, 119 (1955).
[3] H. Watanabe, H. Yamamoto, and K. Ito, J. Phys. Soc. Jpn. **18**, 995 (1963).
[4] G. K. Wertheim, V. Jaccarino, J. H. Wernick, J. A. Seitchik, H. J. Williams, and R. C. Sherwood, Phys. Lett. **18**, 89 (1965).

[5]V. Jaccarino, G. K. Wertheim, J. H. Wernick, L. R. Walker, and S. Arajs, Phys. Rev. **160**, 476 (1967).
[6]Y. Takahashi and T. Moriya, J. Phys. Soc. Jpn. **46**, 1451 (1979).
[7]G. Shirane, J. E. Fisher, Y. Endoh, and K. Tajima, Phys. Rev. Lett. **59**, 351 (1987).
[8]T. E. Mason, G. Aeppli, A. P. Ramirez, K. N. Clausen, C. Broholm, N. Stücheli, E. Bucher, and T. T. M. Palstra, Phys. Rev. Lett. **69**, 490 (1992). For a review of Kondo insulators, see Ref. 15.
[9]L. Mattheiss and D. Hamann, Phys. Rev. B **47**, 13 114 (1993).
[10]Castor Fu, M. P. C. M. Krijn, and S. Doniach (unpublished).
[11]Z. Schlesinger, Z. Fisk, Hai-Tao Zhang, M. B. Maple, J. F. DiTusa, and G. Aeppli, Phys. Rev. Lett. **71**, 1748 (1993).
[12]R. Jullien and R. M. Martin, Phys. Rev. B **26**, 6173 (1982).
[13]Peter S. Riseborough, Phys. Rev. B **45**, 13 984 (1992).
[14]Carlos Sanchez-Castro, Kevin S. Bedell, and Bernard R. Cooper, Phys. Rev. B **47**, 6879 (1993).
[15]G. Aeppli and Z. Fisk, Comments Condens. Matter Phys. **16**, 155 (1992).
[16]R. P. Krentsis, P. V. Gel'd, and G. I. Kalishevich, Izv. Vyssh. Uchebn. Zaved. Chern. Metall. **9**, 161 (1963); P. V. Gel'd and R. P. Krentsis, Fiz. Met. Metalloved. **15**, 63 (1963) [Phys. Met. Metallogr. (USSR) **5**, 59 (1963)]; G. I. Kalishevich, P. V. Gel'd, and R. P. Krentsis, Teplofiz. Vys. Temp. **2**, 16 (1964) [High Temp. (USSR) **2**, 11 (1964)].
[17]D. Pines, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1955), Vol. 1.
[18]V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978), and references therein.
[19]J. D. Thompson and J. M. Lawrence, in *Handbook on the Physics and Chemistry of Rare Earths and Actinides,* edited by K. A. Gschneider, L. Eyring, G. Lander, and G. Choppin (North Holland, Amsterdam, 1994), Vol. 19, p. 385.
[20]R. P. Krentsis, G. I. Kalishevich, P. V. Geld, and L. P. Andreeva, Izv. Vyssh. Vchebon. Zaved. Fiz. **1**, 153 (1972) [Sov. Phys. **15**, 193 (1972)].
[21]D. Mandrus and A. Migliori (unpublished).
[22]J. L. Sarrao, D. Mandrus, A. Migliori, Z. Fisk, and E. Bucher, Physica B **199&200**, 478 (1994).
[23]R. Takke, M. Niksch, W. Assmus, B. Luthi, R. Pott, R. Schefzyk, and D. K. Wohlleben, Z. Phys. B **44**, 33 (1981).
[24]D. Mandrus, J. L. Sarrao, A. Lacerda, A. Migliori, J. D. Thompson, and Z. Fisk, Phys. Rev. B **49**, 16 809 (1994).
[25]B. Luthi, Magn. Magn. Mater. **52**, 70 (1985).
[26]A. Migliori, J. L. Sarrao, W. M. Visscher, T. M. Bell, Ming Lei, Z. Fisk, and R. G. Leisure, Physica B **183**, 1 (1993).
[27]G. P. Zinoveva, L. P. Andreeva, and P. V. Geld, Phys. Status Solidi **23**, 711 (1974).
[28]J. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1962).
[29]B. C. Sales, E. C. Jones, B. C. Chakoumakos, J. A. Fernandez-Baca, H. E. Harmon, J. W. Sharp, and E. H. Volckmann, Phys. Rev. B **50**, 8207 (1994).
[30]C. -H. Park, Z. -X. Shen, A. G. Loeser, D. S. Dessau, D. Mandrus, A. Migliori, J. L. Sarrao, and Z. Fisk (unpublished).