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High pressures and ferromagnetic order in EuB_6

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We have measured the electrical resistivity $\rho(T)$ of single crystals of EuB_6 for temperatures from 1.2 to 300 K, and pressures from 1 bar to 169 kbar. The room temperature resistivity $\rho_{300\,K}$ is dramatically reduced with pressure, while the double ferromagnetic ordering temperatures $T_c^{+,-}$ are strongly enhanced. We argue that magnetic order is driven by the Ruderman-Kittel-Kasuya-Yosida interaction between Eu moments and pockets of carriers at the semimetallic X point. With pressure, the band overlap increases, leading to an increase in carriers at the Fermi surface and the decrease of the spin disorder scattering in the paramagnetic state. [S0163-1829(97)04345-2]

EuB_6 has a long history as a prototypical ferromagnet, due to its crystalline simplicity, as well as its decidedly localized and isotropic Eu moment.[1] Despite its potential as a model system, the relationship between the ferromagnetism and the electronic structure in EuB_6 remains mysterious and controversial. The crystal structure consists of a simple cubic lattice of Eu ions, with B_6 octohedra lying at the cube centers. It was initially proposed on the basis of tight binding calculations that the electronic structure is derived primarily from the hybridization of boron orbitals.[2] In this view, the rare-earth ions are essentially passive electron sources, whose valence serves only to determine the Fermi level. Two electrons are required to completely fill the valence band. Hence, the trivalent hexaborides are expected to be metallic, and divalent hexaborides, insulating.[3,4] More recently, self-consistent calculations have refined this view by including hybridization with $6s$ and $5d$ orbitals of the rare earths.[5–9] The essential features of this electronic structure have been satisfactorily verified by means of de Haas–van Alphen and Shubnikov–de Haas measurements in trivalent rare-earth hexaborides.[10–12] However, the situation for the divalent hexaborides is qualitatively different from the scenario deduced from the tight binding calculations. The fits of the temperature dependent resistivities of EuB_6, SrB_6, and CaB_6 above room temperature, as well as low temperature tunnelling studies find activation gaps of order a few tenths of an eV.[3,13,14] However, none of these compounds show true insulating resistivity at low temperature, indicating the presence of metallic states in the gap.[15] There has been considerable controversy whether these gap states are intrinsic or extrinsic. Shubnikov–de Haas and de Haas–van Alphen measurements[16] on EuB_6 argue for the former, revealing that the Fermi surface consists of extremely small, light mass spherical pockets, which are essentially unaffected by the onset of ferromagnetism. It was proposed that the rare-earth hybridization causes a small band overlap at the X points, rendering the divalent hexaborides semimetallic.[8,9]

EuB_6 is of particular interest, as it is the only rare-earth hexaboride which orders ferromagnetically. What is more, EuB_6 provides the rare possibility of studying magnetic order in a host with exceptionally low carrier concentration and little disorder. Such a study may provide insight into a previously unexplored regime: the crossover from magnetic ordering mechanisms characteristic of magnetic semiconductors, such as the superexchange and the Bloembergen-Rowland interactions, to those characteristic of metals, such as the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. The proximity to this crossover is presumably responsible for the lack of theoretical or experimental consensus on the mechanism responsible for ferromagnetism in EuB_6, or even on the degree of metallicity of EuB_6 itself. If EuB_6 is best described as an insulator, it can be argued[17] in analogy to the EuX ($X=$O, S, Se, Te) compounds that magnetic order occurs by means of a superexchange interaction involving the Eu $5d$ and $4f$ orbitals. However, this view was countered by electron paramagnetic resonance (EPR) line shape analyses showing instead that the dominant interaction is RKKY-like, involving exchange coupling of the rare-earth moments and the small pockets of semimetallic conduction electrons.[18] The Bloembergen-Rowland (BR) interaction is intermediate between these respectively insulating and metallic views. Here, the moments have a virtual interaction by means of their coupling to states lying above the semiconducting gap. Within this model, a reasonable value for the ferromagnetic Weiss constant is predicted for EuB_6, as well as antiferromagnetism in the trivalent rare-earth hexaborides.[19–21] Distinguishing among these three possible ordering mechanisms has previously been complicated by the presence of large numbers of extrinsic carriers. However, recent advances in sample quality make it worthwhile to revisit this issue.

The pressure dependence of the magnetic ordering temperature is one of the most direct means for determining the nature of the magnetic ordering mechanism. Accordingly, we present here the results of electrical resistivity measurements on very high-quality single crystals of EuB_6, which span much larger pressure[22] and temperature[23,24] ranges than have previously been investigated. The pressure dependences of

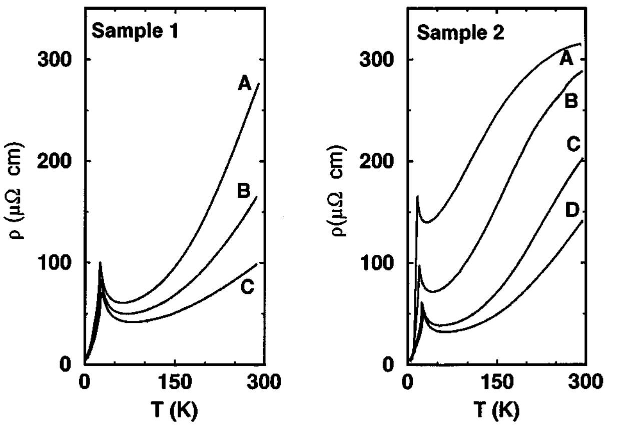

FIG. 1. Electrical resistivity of two single crystals of EuB_6. Applied pressures for sample 1 are A=46 bar, B=79 kbar, C=169 kbar. Applied pressures for sample 2 are A=1 bar, B=13 kbar, C=42 kbar, D=67 kbar.

the underlying moment interactions and carrier concentrations will be discussed from the viewpoint of the superexchange, RKKY, and BR interactions.

Large single crystals of EuB_6 were prepared from an aluminum flux, and were carefully screened for ferromagnetic ordering transitions in the electrical resistivity of at least 15 K. Crystals meeting this criterion were found to have the largest zero-temperature moments and Curie terms in the high-temperature, paramagnetic phase. The samples used have a needlelike morphology, and the electrical resistivity was measured with the current flowing parallel to the needle axis, which is presumed to be a principal crystallographic direction. High-pressure resistivity measurements were carried out in a Bridgman anvil cell, and pressures were determined in situ using a superconducting lead manometer.[25] High-pressure magnetization measurements were performed separately in a special Bridgman cell, employing nonmagnetic ceramic anvils. A small, multiturn coil was wrapped around both the sample and a lead manometer, and the coil voltage was measured using a locking amplifier whose reference voltage was taken from a primary driving coil, located in a low-pressure region of the cell.

The temperature dependences of the electrical resistivity of two different samples of single crystal EuB_6 are presented in Fig. 1, for pressures ranging from ambient pressure to 169 kbar. The resistivity is large at room temperature, decreasing to the cusplike ferromagnetic ordering transition near 15 K. The resistivity in sample 2 at 1.2 K is 4 $\mu\Omega$ cm. Pressure has two major effects on the temperature-dependent resistivity. First, pressure increases the ferromagnetic ordering temperature, consistent with earlier measurements below 10 kbar.[22] Second, pressure substantially reduces the room temperature resistivity.

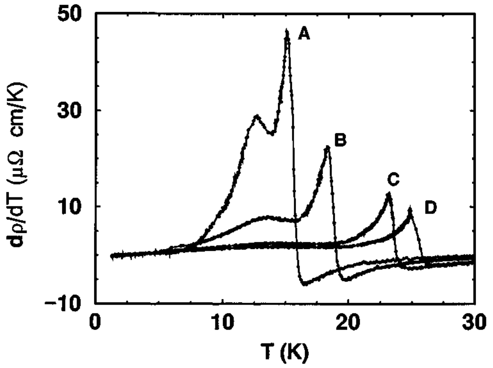

FIG. 2. Temperature dependence of the derivative of the resistivity $\partial\rho/\partial T$ for sample 2. Applied pressures are A=1 bar, B=13 kbar, C=42 kbar, D=67 kbar.

In order to determine the pressure dependence of the ferromagnetic ordering temperature, we have plotted the temperature derivative of the resistivity of sample 2 at different pressures in Fig. 2. The Curie temperature T_c is determined from the maxima in $\partial\rho/\partial T$ for $T = T_c$. The results of Fig. 2 indicate that there are two distinct ordering temperatures in EuB_6, T_c^+ and T_c^-, as has previously been noted in specific heat measurements.[26] At ambient pressure in sample 2, the two transitions occur at $T_c^+ = 15.14 \pm 0.03$ K, and $T_c^- = 12.65 \pm 0.05$ K. The pressure dependences of the two transitions are plotted in Fig. 3 for both samples. Both transition temperatures are enhanced by the application of pressure. T_c^- is initially sensitive to pressure, increasing by about 30% before saturating at pressures of approximately 50 kbar. T_c^+ is more sensitive to pressure than T_c^-, increasing almost a factor of 2 at 169 kbar, showing less tendency to saturate. The upper transition remains equally sharp at all pressures, although the magnitude of the change in resistivity at T_c^+ decreases continuously with increased pressure. In contrast, pressure rapidly broadens the lower transition, as well as suppressing the overall magnitude of $\partial\rho/\partial T$ at all temperatures near the critical points.

We have used high-pressure magnetization measurements to determine that the upper transition T_c^+ corresponds to the onset of a spontaneous magnetization. The results of these measurements appear in Fig. 4, which plots the pickup coil signal as a function of temperature for pressures ranging from 1 bar to 57 kbar. A large, temperature-dependent background from the metallic pressure clamp makes this technique useful primarily for studying sharp transitions, such as ferromagnetic or superconducting transitions. The onset of ferromagnetism in the data of Fig. 4 is associated with the

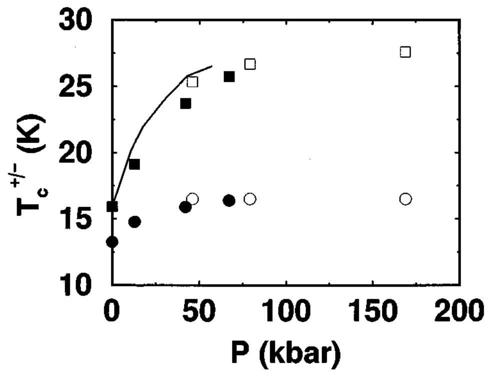

FIG. 3. Pressure dependences of the upper resistive transition T_c^+ (squares) and lower resistive transition T_c^- (circles). Open symbols are for sample 1, filled symbols are for sample 2. Solid line represents the transitions taken from high-pressure magnetization measurements.

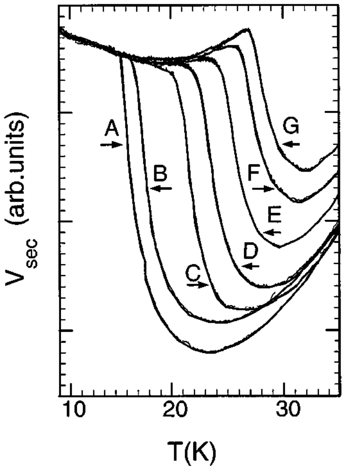

FIG. 4. Temperature dependence of the pickup coil voltage in the vicinity of the ferromagnetic ordering transition of EuB$_6$. Pressures are A (1 bar), B (1 kbar), C (11 kbar), D (18 kbar), E (30 kbar), F (43 kbar), G (57 kbar).

midpoint of the transition in the pickup coil voltage, and the pressure dependence of these transitions is reproduced in Fig. 3. It is clear from this comparison that the higher-temperature transition in the resistivity corresponds to the onset of ferromagnetic order in the magnetization. There is no feature in the pickup signal at the second, lower-temperature resistive transition.

Pressure has a dramatic effect on the room temperature resistivity $\rho_{300\,\mathrm{K}}$ for our two samples. The pressure dependences of $\rho_{300\,\mathrm{K}}$ for both samples appears in Fig. 5. $\rho_{300\,\mathrm{K}}$ is depressed almost a factor of 2 by the application of 67 kbar to sample 2. The continuation of these measurements to higher pressures in sample 1 suggests that $\rho_{300\,\mathrm{K}}$ experiences the same sort of saturation as T_c^+ did above 50 kbar. The pressure dependence, but not its overall magnitude, is in qualitative agreement with two earlier studies of $\rho_{300\,\mathrm{K}}$ at pressures below 100 kbar.[23,24]

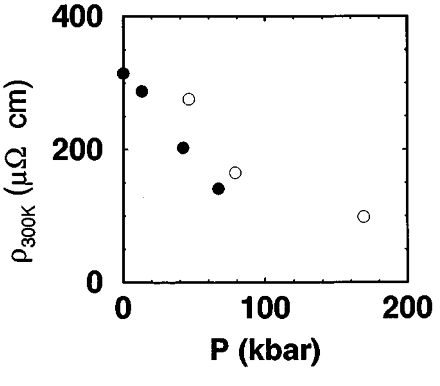

FIG. 5. Pressure dependence of the room-temperature resistivity $\rho_{300\,\mathrm{K}}$. Open symbols are for sample 1, filled symbols are for sample 2.

The pressure dependences of the Curie temperature T_c and the room-temperature resistivity $\rho_{300\,\mathrm{K}}$ provide insight into both the ordering mechanism and its relationship to the electronic structure. It has previously been proposed in the related EuX (X=O,S,Se,Te) compounds that magnetic order occurs via superexchange.[17] Here, the 5d orbitals on neighboring Eu sites overlap, indirectly coupling the f orbitals via the onsite f-d exchange. A point charge model can be constructed for EuB$_6$ to relate the superexchange interaction J to the measured Curie temperature. A Eu ion at the origin has 6 near neighbors at $r=a$, 12 next-nearest neighbors at $r=\sqrt{2}a$, and 6 more neighbors at $r=\sqrt{3}a$:

$$T_c = 2/3S(S+1)[6J_1+12J_2+6J_3]. \tag{1}$$

Here, S is the projection of the Eu spin on the total angular momentum ($S=\frac{7}{2}$), and J_i is the superexchange interaction between the ith Eu neighbors. Since J depends on direct overlap, it is expected that $J_1>J_2>J_3$. In this model, the pressure dependence of T_c in EuB$_6$ arises primarily from that of J_1, just as for the EuX.[27] Using the measured compressibility of EuB$_6$ below 60 kbar,[28] our data indicate an initial $\partial \ln J_1/\partial \ln a \approx -300$. A similar analysis of EuO (Ref. 27) finds a much weaker dependence of J_1 on lattice parameter a, $\partial \ln J_1/\partial \ln a \approx -17$. This anomalously strong dependence of J_1 on lattice parameter was also found in an earlier point charge analysis of EuB$_6$, although the details of our model are different.[22] Even though the degree of covalency and the lattice parameters are admittedly different, it is difficult to believe that the superexchange interaction is more than an order of magnitude more sensitive to lattice parameter in EuB$_6$ than in the EuX. We conclude that a more likely interpretation of this comparison is that magnetic order does not arise from superexchange, at least in EuB$_6$.

It has also been suggested[19–21] that the Bloembergen-Rowland (BR) interaction is responsible for magnetic order in EuB$_6$, at least at low pressures. Here, Eu moments interact indirectly by means of states in the conduction band, whose occupation is given by thermal activation of valence electrons across a gap E_g. The Curie temperature is given by

$$T_c = -3\pi n^2 J^2/k_B E_T S(S+1)\sum_r F(2k_T r) \times \exp[-(2m^* E_g)^{1/2} r/h]. \tag{2}$$

Here, n is the number of conduction electrons per Eu ion, J the exchange interaction between the f moments and the conduction electron spin, S the projection of the Eu spin on the total angular momentum ($S=\frac{7}{2}$), E_T and k_T the energy and wave vector at the top of the valence band, and $F(x)=[x\cos(x)-\sin(x)]/x^4$. The resistivity above room temperature arises from thermal occupation of the conduction band, and is in fact found to be activated, giving $E_g=0.38$ eV at ambient pressure.[13] The pressure dependences of T_c and the room-temperature resistivity $\rho_{300\,\mathrm{K}}$ are assumed to arise primarily from that of E_g. ρ_{RT} decreases from 309 $\mu\Omega$ cm at 1 bar to 100 $\mu\Omega$ cm at our highest pressure of 169 kbar, suggesting that E_g decreases by 30 meV. The ambient pressure value for E_g can be independently deduced from the pressure dependence of T_c^+, which increases from 15.14 to 25.75 K over the same pressure range. This analysis finds an ambient pressure gap $E_g(0)=0.13$ eV, about a factor of 3 smaller than that found in activation fits of the high-temperature resistivity. That is, the pressure dependence of $\rho_{300\,\mathrm{K}}$ is too weak to explain the pressure dependence of T_c, if magnetic order arises from the BR interaction.

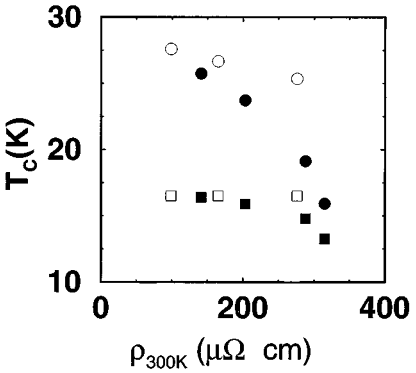

FIG. 6. The upper and lower resistive transitions, T_c^+ (circles) and T_c^- (squares) plotted as a functions of the room-temperature resistivity $\rho_{300\,\mathrm{K}}$. Open symbols are sample 1, filled symbols are sample 2. Pressure is the implicit variable.

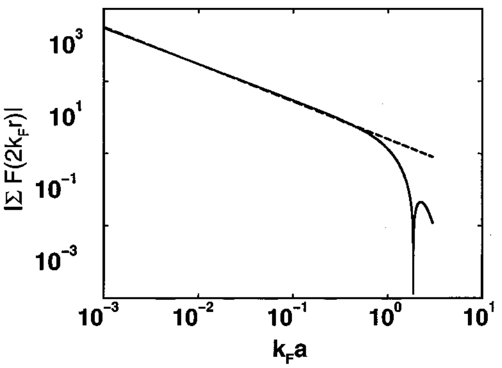

FIG. 7. The magnitude of the spatially dependent part of the RKKY interaction $\Sigma_i F(2k_F r_i)$ as a function of $k_F a$. Dashed line is the relationship $\Sigma_i F(2k_F r_i) \propto (k_F a)^{-1}$, valid for the pressure range accessed in this experiment.

We believe instead that the Eu moments order ferromagnetically in EuB$_6$ by means of the RKKY interaction, involving the small pockets of conduction electrons at the X points found in the band structure calculations.[8,9] The ordering temperature is given by[29,30]

$$T_c = -3\pi n^2 J^2/k_B E_F S(S+1)\sum_i F(2k_F r_i). \qquad (3)$$

E_F and k_F are, respectively, the Fermi energy and Fermi wave vector for the pockets of conduction electrons. The pressure dependence of T_c has two potential sources. In principle, the exchange interaction J is expected to be somewhat enhanced with pressure, as the pressure increases the spatial extent of the conduction electron wave functions. At the same time, pressure would be expected to change the X-point band overlap, consequently modifying the conduction electron concentration. In order to self-consistently determine the pressure dependences of J and n, another measurement is required.

The temperature dependence of the electrical resistivity of EuB$_6$ below room temperature reflects the dominance of spin disorder scattering of a small number of conduction electrons from fluctuating Eu moments. In support of this view, the magnitude of the room-temperature resistivity agrees well with an estimate taken from a crystal field model proposed by Fisk for NdB$_6$.[31] The estimated contribution to the room-temperature resistivity of EuB$_6$ at 1 bar from electron-phonon scattering is less than 3%. In addition, the resistivity at 1 bar drops by almost two orders of magnitude at the magnetic ordering transition. The room temperature resistivity $\rho_{300\,\mathrm{K}}$ gives an independent measurement of J and n since[32–34]

$$\rho_{300\ \mathrm{K}} = (3\pi^2 Nm/he^2 E_F)J^2(g-1)^2 S(S+1). \qquad (4)$$

Here, N is the number of atoms per unit volume, and g the Landé g factor. By combining Eqs. (3) and (4), we can uniquely determine the pressure dependences of J and n.

It is straightforward to show that the pressure dependence of T_c is not dominated by the pressure dependence of J. If J were the dominant pressure effect, T_c and $\rho_{300\,\mathrm{K}}$ would be linearly related since both are proportional to J^2. $T_c^{+,-}$ are plotted as a function of $\rho_{300\,\mathrm{K}}$ in Fig. 6, with pressure as the implicit variable. Since $T_c^{+,-}$ both increase with pressure and $\rho_{300\,\mathrm{K}}$ decreases with pressure, there is not even qualitative agreement for the relationship $T_c^{+,-} \propto \rho_{300\,\mathrm{K}}$. Studies[35] of pair-breaking rates due to rare-earth impurities in superconducting YB$_6$ show almost no variation of J with lattice constant, an observation born out by atomic overlap calculations.[36] The situation is somewhat more complex for EuB$_6$, as our analysis will show that the electron concentration n, and consequently the local moment-conduction electron wave function overlap are pressure dependent. However, we will show that the variation in J is relatively weak for the electron concentrations found in pressurized EuB$_6$, and is not responsible for the pressure dependence of T_C, except perhaps at the lowest pressure where n is changing the most quickly.

In order to determine the pressure dependence of n, we must first explicitly calculate the oscillatory RKKY function $\Sigma_j F(2k_F r_i)$ for EuB$_6$ and determine its primary dependence on $k_F a$. A Eu ion at the origin has 6 near neighbors at $r = a$, 12 next-nearest neighbors at $r = \sqrt{2}a$, and 6 more neighbors at $r = \sqrt{3}a$. $\Sigma_i F(2k_F r_i)$ is negative, signifying ferromagnetic interactions for $k_F a < 1.86$. This value of $k_F a$ corresponds to a critical conduction electron density of 0.22

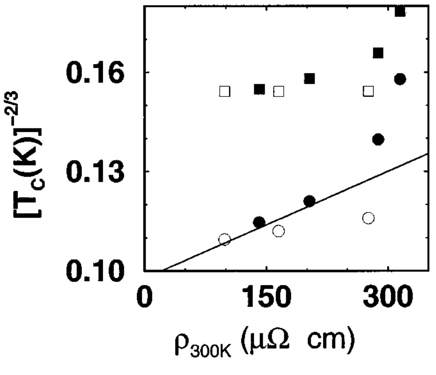

FIG. 8. Plot of $(T_c^{+,-})^{-2/3} - \propto n^{-2/3} \propto \rho_{300\,\mathrm{K}}$. Circles represent the upper transition T_c^+, squares the lower transition. Open symbols represent sample 1, filled symbols sample 2. Line is a guide for the eye.

electrons per Eu. Photoemission[37] and Mössbauer[38] measurements of EuB_6 samples from the same batch as our resistivity samples place a much lower bound on the magnitude of deviations of the Eu valence from 2. Ambient pressure, room-temperature Hall effect[39] and low-temperature Fermi surface measurements[16] suggest a very small electron concentration $n \approx 10^{-3}$ electrons per Eu. That is, for the pressures accessed in our experiment the number of conduction electrons per Eu is certainly much less than one, and $k_F a \ll 1.86$. The absolute value of $\Sigma_i F(2k_F r_i)$ is plotted as a function of $k_F a$ in Fig. 7. The RKKY interaction decreases monotonically as $(k_F a)^{-1}$ over the range of $k_F a$ likely to be accessed in our high-pressure measurements. The leading pressure dependences of T_c and $\rho_{300\,\mathrm{K}}$ consequently are

$$T_c \sim J^2 n(P), \quad \rho_{300\,\mathrm{K}} \sim J^2/n^{2/3}(P). \tag{5}$$

Since both T_c and $\rho_{300\,\mathrm{K}}$ depend on J in the same way, we can use these expressions (5) to test whether the pressure variations in both reflect the pressure dependence of the electron concentration. If so, the form of the RKKY interaction implies $\rho_{300\,\mathrm{K}} \propto T_c^{-2/3}$. As can be seen from Fig. 8, the data are consistent with the upper transition T_c^+, but not the lower transition T_c^- being driven by the RKKY interaction. In this view, the pressure dependence of T_c^+ mirrors that of the electron concentration n, which we deduce approximately doubles over the pressure range explored in our measurements. Calculations of the band overlap in EuB_6 as a function of pressure, using measured lattice compressibilities would be a very useful test of this scenario.

Our high-pressure measurements indicate that ferromagnetic order in EuB_6 is driven by an RKKY interaction between the localized Eu moments, and the very dilute pocket of conduction electrons arising from semimetallic band overlap. As pressure increases this overlap, the concentration of these carriers increases, and is simultaneously responsible for the gradual depression of spin disorder scattering in the paramagnetic state.

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[1] See, for instance, Z. Fisk, D. C. Johnston, B. Cornut, S. von Molnar, S. Oseroff, and R. Calvo, J. Appl. Phys. **50**, 1911 (1979).

[2] H. C. Longuet-Higgins and M. Roberts, Proc. R. Soc., Ser. A **224**, 336 (1954).

[3] R. W. Johnson and A. H. Daane, J. Chem. Phys. **38**, 425 (1963).

[4] J. Etorneau, J.-P. Mercurio, R. Naslain, and P. Hagenmuller, J. Solid State Chem. **2**, 332 (1970).

[5] P. F. Walch, D. E. Ellis, and F. M. Mueller, Phys. Rev. B **15**, 1859 (1977).

[6] P. G. Perkins, D. R. Armstrong, and A. Breeze, J. Phys. C **8**, 3558 (1975).

[7] A. Hasegawa and A. Yanase, J. Phys. F **7**, 1245 (1977).

[8] A. Hasegawa and A. Yanase, J. Phys. C **12**, 5431 (1979).

[9] S. Massidda, A. Continenza, T. M. de Pascale, and R. Monnier, Z. Phys. B **102**, 337 (1997).

[10] A. J. Arko, G. Crabtree, D. Karim, F. M. Mueller, L. R. Windmiller, J. B. Ketterson, and Z. Fisk, Phys. Rev. B **13**, 5240 (1976).

[11] A. P. J. van Deursen, Z. Fisk, and A. R. de Vroomen, Solid State Commun. **44**, 609 (1982).

[12] Y. Onuki, A. Umezawa, W. K. Kwok, G. W. Crabtree, M. Nishihara, T. Yamazaki, T. Omi, and T. Komatsubara, Phys. Rev. B **40**, 11 195 (1989).

[13] J. B. Goodenough, J.-P. Mercurio, J. Etorneau, R. Naslain, and P. Hagenmuller, C. R. Seances Acad. Sci., Ser. C **277**, 1239 (1973).

[14] B. Amsler, Z. Fisk, J. L. Sarrao, S. von Molnar, M. W. Meisel, and F. Sharifi (unpublished).

[15] H. R. Ott, M. Chernikov, E. Felder, L. Degiorgi, E. G. Moshopoulou, J. L. Sarrao, and Z. Fisk, Z. Phys. B **102**, 337 (1997).

[16] M. C. Aronson, B. Brandt, J. L. Sarrao, and Z. Fisk (unpublished).

[17] P. Wachter, in *Handbook on the Physics and Chemistry of the Rare Earths*, edited by K. A. Gschneidner and L. Eyring (North-Holland, Amsterdam, 1979), Vol. 2, p. 540.

[18] W. S. Glaunsinger, Phys. Status Solidi B **70**, K151 (1975); W. S. Glaunsinger, J. Phys. Chem. Solids **37**, 51 (1976).

[19] Z. Fisk, Phys. Lett. **34A**, 261 (1971).

[20] R. M. Xavier, Phys. Lett. **25A**, 244 (1967).

[21] A. M. de Graaf and R. M. Xavier, Phys. Lett. **18**, 225 (1965).

[22] C. N. Guy, S. von Molnar, J. Etorneau, and Z. Fisk, Solid State Commun. **33**, 1055 (1980).

[23] J. M. Leger, A. Percheron-Guegan, and C. Loriers, Phys. Status Solidi A **60**, K23 (1980).

[24] M. M. Korsukova, N. N. Stepanov, E. V. Gontcharova, V. N. Gurin, S. P. Nikanorov, and I. A. Smirnov, J. Less-Common Met. **82**, 211 (1981); V. A. Sidorov, N. N. Stepanov, O. B. Tsiok, L. G. Khvostantsev, I. A. Smirnov, and M. M. Korsukova, Sov. Phys. Solid State **33**, 720 (1991).

[25] T. F. Smith, C. W. Chu, and M. B. Maple, Cryogenics **9**, 53 (1969).

[26] T. Fujita, M. Suzuki, and Y. Isikawa, Solid State Commun. **33**, 947 (1980).

[27] D. B. McWhan, P. C. Souers, and G. Jura, Phys. Rev. **143**, 385 (1966); T. R. McGuire, B. E. Argyle, M. W. Shafer, and J. S. Smart, J. Appl. Phys. **34**, 1345 (1963); M. R. Oliver, J. A. Kafalas, J. O. Dimmock, and T. B. Reed, Phys. Rev. Lett. **24**, 1064 (1970).

[28] H. E. King, S. J. LaPlaca, T. Penney, and Z. Fisk, in *Valence Fluctuations in Solids*, edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981), p. 333.

[29] K. Yosida, Phys. Rev. **106**, 893 (1957).

[30] P. G. de Gennes, J. Phys. Radium **23**, 510 (1962).

[31] Z. Fisk, Solid State Commun. **18**, 221 (1976).

[32] L. L. Hirst, Solid State Commun. **5**, 751 (1967).
[33] T. Kasuya, Prog. Theor. Phys. **16**, 58 (1956); **22**, 227 (1959).
[34] P. G. de Gennes and J. Friedel, J. Phys. Chem. Solids **4**, 71 (1958).
[35] Z. Fisk, B. Matthias, and E. Corenzwit, Proc. Natl. Acad. Sci. USA **64**, 1151 (1969).
[36] F. Milstein and L. B. Robinson, Phys. Rev. Lett. **18**, 308 (1967).
[37] J. Clack, J. Denlinger, J. W. Allen, J. L. Sarrao, and Z. Fisk (unpublished).
[38] M. Abd-Elmeguid, R. D. Taylor, and Z. Fisk (unpublished).
[39] J. M. Tarascon, J. Etorneau, P. Dordor, P. Hagenmuller, M. Kasaya, and J. M. D. Coey, J. Appl. Phys. **51**, 574 (1980).