Complex magnetic states of the heavy fermion compound CeGe

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(Submitted April 3, 2012)
Fiz. Nizk. Temp. **38**, 821–827 (July 2012)

The intermetallic compound CeGe exhibits unusual magnetic behavior owing to the interplay between Kondo and antiferromagnetic coupling. This system is interesting because the Kondo temperature is close to the Néel temperature, so there is a close competition between the low-temperature interactions, which can be tuned by varying external parameters such as pressure and applied magnetic field. Interestingly, magnetization measurements up to 12 kbar reveal that the Néel temperature is not affected by pressure. Measurements of the electrical resistivity show, however, that the sharp upturn below T_N is sensitive to pressures up to 15 kbar. This suggests that pressure may change the complex antiferromagnetic spin structure. The validity of an explanation based on the magnetic superzones seen in the rare earths is discussed here. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4734012]

1. Introduction

As an antiferromagnetic (AFM) heavy fermion (HF) system, CeGe would appear to fit into a well studied physical framework: that of a competition between the Kondo interaction and RKKY exchange as demonstrated in the famous Doniach phase diagram.[1] Doniach showed the possibility of a system in which there could be an antiferromagnetic state and a heavy fermion Fermi liquid state with a second order phase transition from one to the other that would occur as the dominant exchange and/or the density of states were modified. CeGe is relatively understudied, mainly because of difficulties in sample preparation. CeGe displays unexplained features in the temperature dependence of its resistivity. Below the Néel temperature there is a significant upturn in the resistivity followed by a peak a few Kelvin lower. To account for these features, some exotic magnetic states have been proposed. We discuss resistivity under pressure in this system in terms of an interplay among the magnetic interactions that exist in heavy fermion systems. More specifically the possibility of magnetic superzones in the material and their effect on the pressure and field dependence is considered.

Among the Ce intermetallic binary alloys, some that have received less attention because of their apparently simple underlying physics. This true of CeGe alloy. It was characterized in the 1960's (Ref. 2) as a simple antiferromagnet with a well-defined Curie-Weiss law yielding an effective magnetic moment close to that of the free ion value and a Néel temperature $T_N \sim 10\,\mathrm{K}$. Recent studies have, however, revealed a richer phenomenology for this alloy that suggests a greater complexity than previously reported. On one hand, μSR spectra indicate a complex antiferromagnetic spin structure.[3] On the other, magnetization measurements show a strong irreversibility between the field-cooled (FC) and zero-field-cooled (ZFC) curves at low temperatures and a quite broadened metamagnetic transition.[4] The exotic behavior of the resistivity below T_N provides further evidence for such a complex magnetic ground state.[3] These studies show that resistivity undergoes a sharp upturn at T_N which is quenched above 70 kOe. Such anomalous behavior has been attributed to the formation of magnetic superzone gaps in the antiferromagnetic phase.[3]

A detailed study by means of heat capacity allowed the Kondo hybridization in this alloy, as well as the drop in the Ce magnetic moment, to be quantified.[4] The analysis performed in that paper resulted in a magnetic moment of $1.1\,\mu B$, the same as that derived from neutron diffraction,[5] which indicates a non-negligible Kondo effect. Indeed, further analysis yields a value for the T_K/T_N ratio of 0.75. Since

T_N and T_K are very close, CeGe is a good candidate for altering the balance between the Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange interaction and the Kondo screening. Changes in this balance should show up as variations in T_N. In this paper we report magnetization and resistivity measurements down to very low temperatures with applied pressures of 12 and 15 kbar, respectively.

The magnetic contributions to the specific heat and entropy have a lambda peak and kink respectively at the Néel temperature. Estimates of the Kondo temperature from these data are $T_K \sim 8.1$ K and 7.1 K. The jump in specific caused by magnetic ordering can be used to estimate the magnetic moment and yields a value of 1.1 μB in agreement with neutron data.[5] Compared to the free ion value for Ce^{3+} of 2.14 μB, this also suggests a very substantial Kondo effect.

2. Experimental details

The samples for the present experiments were polycrystals prepared by carefully melting together stoichiometric amounts of pure Ce and Ge in an arc furnace in an inert Ar atmosphere. Care was taken to compensate for the weight loss of the more volatile Ge. The ingot was flipped several times and remelted to ensure good homogeneity. Details about the preparation, crystallography, and quality control of the samples have been reported previously.[4] Magnetization measurements were made using a miniature CuBe piston clamp cell in a Quantum Design Superconducting Quantum Interference Device (SQUID) magnetometer (MPMS7). The superconducting transition of tin served as pressure gauge. The resistivity measurements were made out in a piston cylinder clamp cell using a standard 4-terminal low-frequency ac technique in an adiabatic demagnetization refrigerator with low-noise transformers to enhance the signal-noise ratio. An *n*-pentane-isopentane mixture was used as the pressure medium.

3. Results and discussion

Figure 1(a) is a plot of the dc susceptibility (M/H) measured at 10 kOe up to 12 kbar. The data have been transformed to take account of the CuBe pressure cell background. At this magnetic field there is no irreversibility between the ZFC and FC curves. The peak defining the magnetic ordering temperature T_N is well-defined even under external pressure. The application of pressure hardly affects the position of the peak which lies around 10.8 K.

At lower fields, however, there is a strong irreversibility in FC and ZFC with at least two different contributions to the ZFC curve and a strong increase of the FC susceptibility below T_N.[4] This irreversibility has been attributed to a very small ferromagnetic component in the magnetic structure. In order to explore whether there are any pressure-induced effects in the magnetic structure, we show the variation in the isothermal magnetization at 2 K up to 70 kOe in Fig. 1(b). At ambient pressure we observe a curvature in the M-H plot near 20 kOe which is a signature of antiferromagnetism in zero field. This curvature extends over a wide range of fields, indicating a progressive flipping of the magnetic moments. This curvature is slightly less for $P = 12$ kbar, the highest applied pressure. This suggests that pressure induces subtle differences in the magnetic structure.

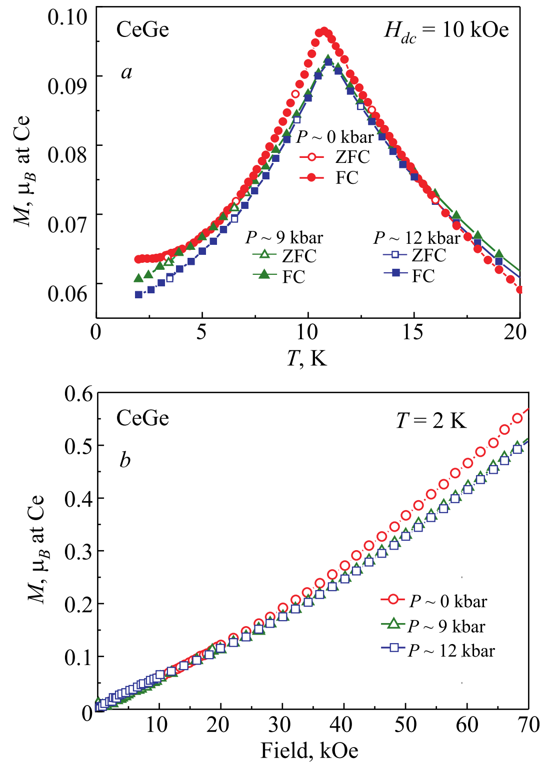

FIG. 1. Dc susceptibility curve measured for CeGe in an applied magnetic field of 10 kOe up to 12 kbar (a). Isothermal magnetization behavior of CeGe under pressure at 2 K. The curvature seen at 20 kOe indicates the onset of the flipping process. The smooth curves are guides to the eye (b).

The application of hydrostatic pressure should affect the strength of the RKKY interaction by modifying the interatomic distances. The balance between the magnetically ordered state and the Kondo lattice will be shifted. Comparing the effect of hydrostatic pressure and that of an applied magnetic field will provide information on the relevant physics.

It is clear from Fig. 2 that pressure and magnetic field are not equivalent as tuning parameters. Although both reduce the peak height because of magnetic superzones, the behavior of the resistivity is quite different in each case. Applying a field reduces the resistivity everywhere below T_N and has the most effect on the peak itself. Applying a pressure increases the resistivity over a wide range of temperatures and has the largest effect at T_N, thereby appearing to suppress the peak.

Figure 3 shows that while an applied field suppresses the peak associated with the magnetic superzones and also suppresses the Néel temperature, application a pressure actually enhances T_N slightly, and also reduces the height of the peak. The enhancement is small, $\sim$20 mK$\cdot$kbar^{-1}. T_N is taken to be the point at which the gradient of $\rho(T)$ becomes negative as the temperature is reduced.

The changes in the low temperature resistivity with applied field and pressure are shown in Fig. 4 with ρ_0 subtracted; it is clear that pressure increases the curvature while an applied field reduces it to the point where it is very nearly linear.

The residual resistivity is enhanced by applying pressure and reduced by applying a magnetic field (Fig. 5).

The resistivity of a metal is determined by the number of available charge carriers and the total scattering rate of

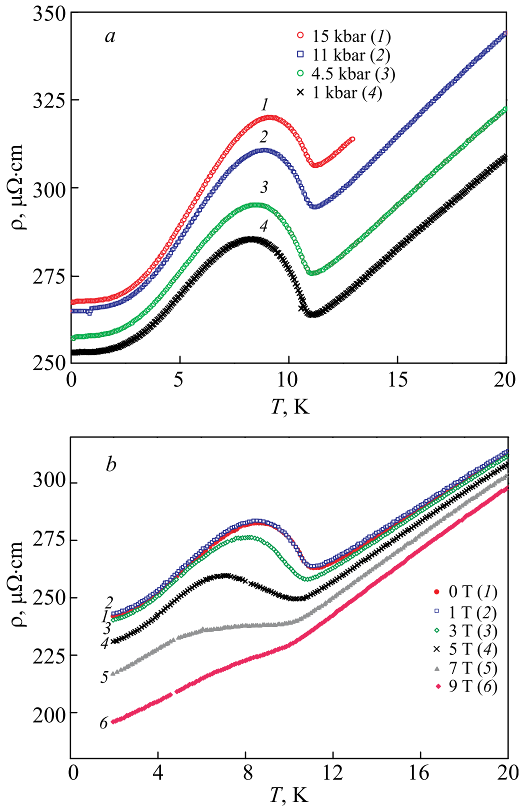

FIG. 2. Pressure (a) can be seen to affect the resistivity in a number of ways: the residual resistivity is raised, the peak height above the curve is suppressed, and the Néel temperature is slightly enhanced. The effect of a field is different[6] (b). The peak is suppressed and the residual resistivity is reduced.

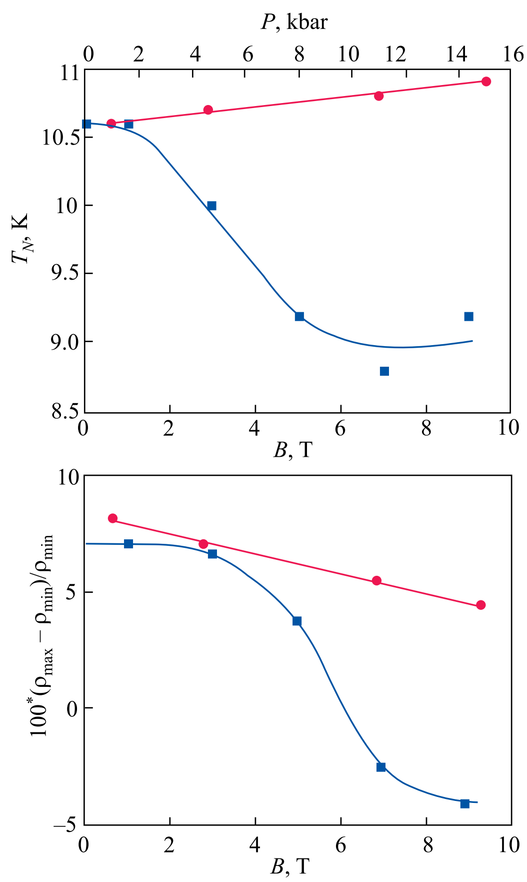

FIG. 3. The effects of applied field and pressure on the Néel temperature (a) and peak height (b). In both plots the red circles (•) correspond to the pressure axis and the blue squares (■) to the applied field.

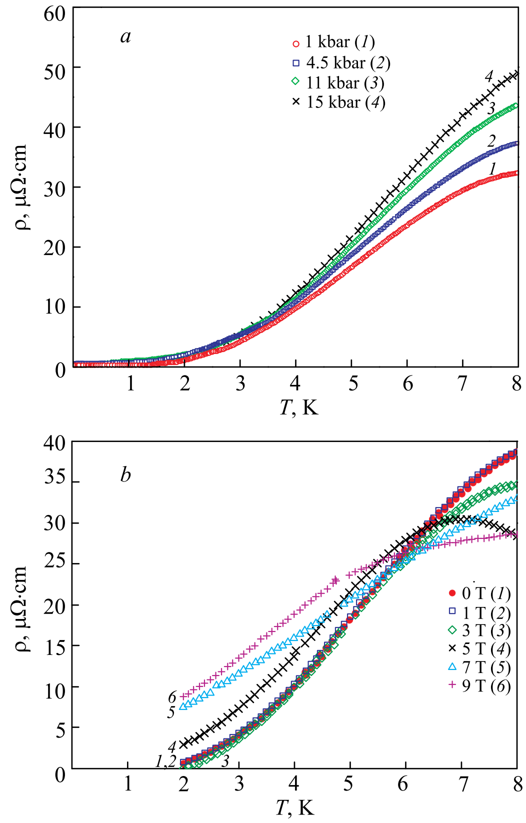

FIG. 4. By subtracting the residual resistivity it is easier to see that, while applying pressure does increase the curvature, applying a magnetic field changes the behavior of the resistivity more drastically.

the carriers. The overall scattering rate is the sum of the scattering rates associated with a number of different processes that will, in general, have different dependences on temperature, pressure, applied magnetic field, etc.:

$$\rho(T) \sim \frac{\tau^{-1}}{n}, \tag{1}$$

$$\frac{1}{\tau_{\mathrm{tot}}} = \frac{1}{\tau_{\mathrm{imp}}} + \frac{1}{\tau_{\mathrm{ep}}} + \frac{1}{\tau_{\mathrm{em}}} + \frac{1}{\tau_{\mathrm{Kon}}}. \tag{2}$$

The first of the above scattering rates, τ_{imp}, is attributed to impurities and crystal imperfections. This rate is assumed to be independent of temperature. The extrapolated value, ρ_0, is entirely a result of this scattering mechanism, since all other scattering mechanisms will eventually vanish at absolute zero. The second term, τ_{ep}, represents the scattering rate associated with electron-phonon interactions. This involves the transfer of momentum to the crystal lattice by absorption and creation of phonons by conduction electrons. Here there are two distinct processes: normal scattering where an electron is scattered by a small angle from one part of the Fermi surface to another, and Umklapp scattering, where an electron is scattered across the Brillouin zone boundary to an equivalent state on the other side of the Fermi surface whence it started. Umklapp processes are, therefore, large angle scattering events that make a significant contribution to the resistivity.

τ_{em} corresponds to scattering of conduction electrons with the absorption and emission of magnetic excitations.

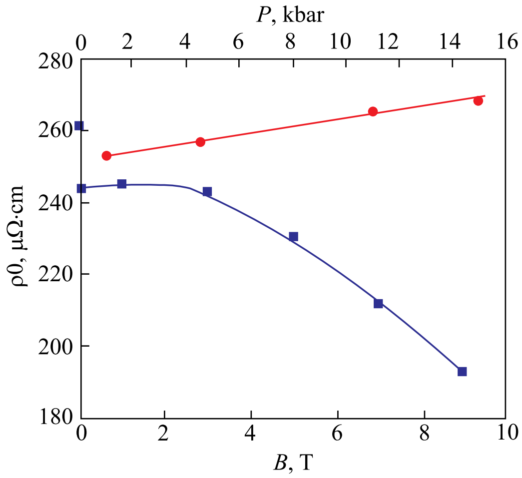

FIG. 5. Effect of pressure and field on ρ_0. The red circles (●) correspond to the pressure axis and the blue squares (■) to the applied field.

Again, these scattering events can be normal or Umklapp processes.

Finally, $\tau_{\rm Kon}$ gives the rate of scattering owing to partially screened local moments. These local moments are antiferromagnetically coupled to the electron cloud that surrounds them and screening a substantial fraction of the moment. This screening becomes more complete as the temperature is lowered, so that the resistivity increases as the temperature is lowered. Neutron diffraction and specific heat studies have confirmed that the Kondo effect is non-negligible in CeGe. The observed moment is half that of the free cerium ion, suggesting that the moment has been substantially screened by the conduction electrons. The Kondo lattice (KL) model discussed by Coqblin, *et al.*,[7] suggests that the KL state must be in competition with long range magnetic order (LRO) but may coexist with short range order (SRO).

This fine balance of the energy scales is one of the fundamental reasons for the interest in heavy fermion systems. It would be expected that in this situation, a relatively small change in any tuning parameter might lead to large changes in the system properties. Indeed, the application of field does appear to cause a large change in the resistivity of the system. It is possible, in a very simple way, to compare the energies delivered to the system through increases in temperature, magnetic field and hydrostatic pressure. In practical units, and very approximately, the thermal energy is given by Boltzmann's constant: $k_B \sim 9\cdot 10^{-5}$ eV·K^{-1}. This compares with the Bohr magneton: $\mu_B \sim 6\cdot 10^{-5}$ eV·T^{-1}. The energy equivalent of applied pressure is slightly less trivial to estimate; the work done on a test cube with realistic modulus of compression corresponds to an energy of $\sim 9\cdot 10^{-5}$ eV·kbar^{-1}. The fact that the effect of pressure is markedly less than that of a magnetic field suggests, therefore, that this approximation is deficient. This is not surprising, as this very simple comparison neglects any effects arising from the strongly correlated electrons in the system. A more revealing comparison would require calculating the dependence of the lattice spacing on the exchange interaction. Neutron scattering may well be able to reveal this relationship and shed light on the apparent stability of the magnetic state under pressure.

A discussion of the effect of pressure on the resistivity and what this can tell us about the balance of the energy scales in this system falls naturally into two parts: above and below the magnetic ordering temperature T_N. Above this temperature the system has a unit cell and, therefore, a Brillouin zone that corresponds to the primitive unit cell of the crystal. Once the system becomes antiferromagnetically ordered, the real space unit cell is doubled, and the Fermi Surface is reduced and its shape changed.

3.1. Temperatures above the Néel temperature

To understand the effect of pressure on the resistivity of CeGe it is necessary to consider how an applied pressure changes the magnetic interactions in the system. There are two mechanisms to consider: Kondo screening and the RKKY interaction. The competition between these two energy scales is usually discussed in terms of the Doniach phase diagram,[1] where J is the magnetic exchange between localized f electrons and the conduction electrons. In cerium based compounds the pressure effectively squeezes one f electron out of the localized f orbital and into the conduction band, eventually reducing the contribution that can be made to the local moment to zero. In the intermediate regime, the application of pressure serves to increase the hybridization between the f electrons and the charge carriers. This enhances the strength of the Kondo scattering interaction and leads to increased resistivity. This can also provide an explanation for the rising Néel temperature; the enhanced scattering increases the entropy of the system, making it more favorable for the magnetic ordering to which the system is already prone. It would, therefore, be reasonable to look for enhanced magnetic susceptibility; however, this is not observed. The effect owing to the depletion of the f orbital may well be dominant.

The fact that the ratio $T_K/T_N \sim 0.75$ means that we can place CeGe at atmospheric pressure, on the Doniach phase diagram somewhere near the apex of T_N. This may well explain why T_N is relatively insensitive to applied pressure and actually increases slightly. This does not mean that the applied pressure has no effect on the system in general—it just so happens that the effects on the Néel temperature are essentially cancelled out in this pressure range. Many cerium based heavy fermion compounds have been studied under pressure. It is reasonably common for the Néel temperature to start at around 10 K and increase slightly with applied pressure before being suppressed strongly. One possible indicator of closeness to the tipping point at which the Kondo lattice suppresses the antiferromagnetism is the electronic specific heat factor γ. In general, those materials on the left of the Doniach diagram display low values of γ; in other words, the heavy fermions are quite light and the Kondo effect is negligible. Usually, materials with very large γ do not order magnetically and are dominated by the Kondo interaction. In CeGe, specific heat measurements give $\gamma \sim 260$ mJ·K^2·mol. This is somewhere in the middle of the observed range. Work on $CeSi_{1-x}Ge_x$ (Ref. 5) has shown that introducing the larger germanium atom into the lattice leads to a volume expansion of the unit cell that is smaller than the extra volume taken up by the germanium, i.e., to an effective increase of pressure. As x is increased, the Néel temperature rises from ~6–10 K as would be expected if the system were following the standard Doniach picture.

3.2. Temperatures below the Néel temperature

As the temperature is reduced towards T_N and the system approaches the second order transition to the antiferromagnetic state, the magnetic fluctuations will become increasingly long-lived and long-ranged. When the system is ordered antiferromagnetically, magnetic fluctuations are frozen out above the transition. This means a reduction in scattering rates which, if this were the dominant effect, would lead to a reduction in resistivity (see Ref. 8). However, noted above, this is often not the case and the resistivity increases just below the transition. The Fermi surface is fundamentally changed by magnetic ordering. The unit cell is doubled in the case of a simple antiferromagnet. This can either be viewed as a reduced Brillouin zone or as the original Brillouin zone but with gaps. Either way, it is clear that the carrier concentration is reduced. The details of the Fermi surface then become the crucial parameters determining the behavior of the system at the transition. Unfortunately, theoretical calculations based on detailed Fermi surfaces are in short supply. For example, it is not known what effect applying a magnetic field will have on the shape of the Fermi surface of a band antiferromagnet with regard to the reduction in carriers and the effects this will then have on the exchange interaction and electron-electron scattering. Likewise, the exact effects of pressure on the lattice parameters and, thereby, on the band structure and exchange, density of states, and scattering rates are not known for a realistic antiferromagnetic Fermi surface.

In a paper published in 2005,[9] Monthoux and Lonzarich considered a tight binding band appropriate for Sr_2RuO_4. The effective interaction, assumed to be magnetic, was then studied for different band filling factors. They showed that even in their relatively simple model the effective interaction could have attractive regions in k space. If a Cooper pair which principally samples these regions can exist, then an instability to superconductivity may exist. In this single band it was found that the interaction may be attractive and have different symmetries, depending sensitively on the filling of the band. This calculation should make us aware that the intricacies of the electronic band structure may very well contain the necessary physics to account for many features seen in the transport and susceptibility properties of strongly correlated systems.

3.3. Magnetic superzones?

The account of resistivity anomalies in the heavy rare earths (Gd-Tm) given by Elliott and Wedgwood[10] in 1963 is based on magnetic ordering with a spiral spin structure. This kind of ordering has a lower symmetry than the hexagonal structure of these rare earths and leads to new boundaries in the Brillouin zone which distort the Fermi surface. In this theory, the shape of the Fermi surface and the symmetry of the crystal play an important role in determining the effect of magnetic ordering on the electron scattering and hence the resistivity. Calculations by Ellerby, *et al.*, in Ref. 11 based on the theory of Elliott and Wedgwood, explain the effect of an applied magnetic field on the

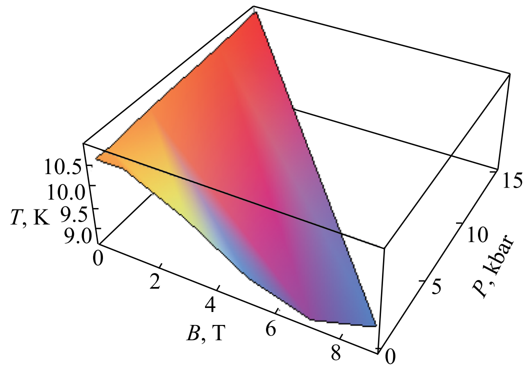

FIG. 6. The Néel temperature decreases significantly when a magnetic field is applied, but is only slightly enhanced when pressure is applied. Here $dT_N/dP \sim 0.02\,\mathrm{K{\cdot}kbar^{-1}}$. Although this change is very small, it is comparable to that in other heavy fermion magnets.[12] The effect of applied pressure on the shape of the resistivity is marked. The peak height and residual resistivity are, respectively, substantially lowered and raised.

resistivity anomaly in thulium. The form of the resistivity of Tm is very similar to that seen for CeGe. There are, however, important differences. Neutron diffraction measurements in Tm have confirmed that the magnetic structure is of the type needed to make magnetic superzones very important for describing the transport, i.e., it has a lower symmetry than the crystal. Thulium has an hexagonal crystal structure and a ferrimagnetic ordering at low temperatures. These are also generally to be found in the rare earths that have magnetic superzones. CeGe is not hexagonal, and neutron diffraction has not revealed any ferromagnetic component of the magnetization. In addition, cerium is not a heavy rare earth.

Accounting for the pressure and field dependences of the resistivity is a key test for the applicability of these two models to this system. If it is found that only the magnetic superzone model can account for the observed data, then the magnetic ground state of this system would warrant further study by neutron diffraction.

4. Conclusions

The pressure-magnetic field phase diagram is plotted in Fig. 6.

The changes in the form of the resistivity can be explained in terms of the various scattering rates and changes to the carrier concentration that occur in a system caught in a fine balancing act between two states with comparable energy scales. The curvature of the isothermal magnetization associated with the zero-field AFM state is suppressed when a pressure is applied. This supports the observation that pressure alters the underlying magnetic ground state of CeGe. The idea of magnetic superzones remains enigmatic in CeGe. Calculations of the effect of the extra zone boundaries and how this can be distinguished from the effects of a commensurate AFM transition are needed. With these models in place it may be possible to determine the dominant physical processes that account for the results presented in this study.

We thank Gil Lonzarich, Cheng Liu, Mark Dean, Mike Sutherland, Stephen Rowley, Valentina Sirenko and Victor Eremenko for useful discussions. This work was supported by EPSRC, the European ECOM COST Action P16 ESF Intelbiomat and the Spanish MEC. The authors wish to thank the following organizations for financial support—C. R. S. Haines acknowledges Corpus Christi College, S. S. Saxena acknowledges Jesus College.

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