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Complex magnetic states of heavy fermion compound CeGe

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The intermetallic compound CeGe exhibits unusual magnetic behavior due to the interplay between the Kondo and the antiferromagnetic coupling. This particular system is interesting because the Kondo temperature is close to the Néel temperature, resulting in a close competition between the low-temperature interactions, which can be tuned by means of 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, however, show that the sharp upturn appearing 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.

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1. Introduction

As an antiferromagnetic (AFM) heavy fermion (HF) system, CeGe would appear to fit into a well studied physical framework; that of the competition between the Kondo interaction and the 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, due mainly to 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. A desire to account for these features has led to the proposal of some exotic magnetic states. We discuss resistivity under pressure in this system in terms of the interplay of magnetic interactions present in the 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 there are some that have received less attention due to their apparently simple underlying physics. This is the case of the CeGe alloy. It was characterized in the 1960's [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 $T_N \sim 10$ K. Recent studies , however, have shown a richer phenomenology on this alloy suggesting a larger degree of complexity than was previously reported. On the one hand, μSR spectra indicate a complex antiferromagnetic spin structure [3]. On the other hand, the 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]. According to such a study, resistivity shows a sharp upturn at T_N which is found to be quenched above 70 kOe. Such anomalous behavior was 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 existent in this alloy, as well as the Ce magnetic moment reduction to be quantified [4]. The analysis performed in that work resulted in a magnetic moment of 1.1 μ_B, the same as that reported 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 to alter the balance between the Ruderman–Kittel–Kasuya–Yosida (RKKY) exchange interaction and the Kondo screening. The changes of this balance should be reflected in the variations of T_N. In this paper we report magnetization and resistivity measurements down to very low temperature at applied pressures of 12 kbar and 15 kbar respectively.

Magnetic contributions to the specific heat and entropy show 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 heat due to the magnetic ordering can be used to estimate the magnetic moment and yields a value of 1.1 μ_B in agreement with neutron data [5]. Compared to the free ion value for Ce^{3+} of 2.14 μ_B this also suggests a very substantial Kondo effect.

2. Experimental details

The samples in the present work are polycrystals prepared by carefully melting together stoichiometric amounts of pure Ce and Ge in an arc furnace under 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 previously reported [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. Resistivity measurements were carried out in a piston cylinder clamp cell using a standard 4-terminal low-frequency ac technique in an adiabatic demagnetisation refrigerator with low-noise transformers to enhance the signal-noise ratio. A mixture of *n*-pentane-isopentane were used as the pressure medium.

3. Results and discussion

In Fig. 1,*a* we present 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 such a 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, with its position around 10.8 K.

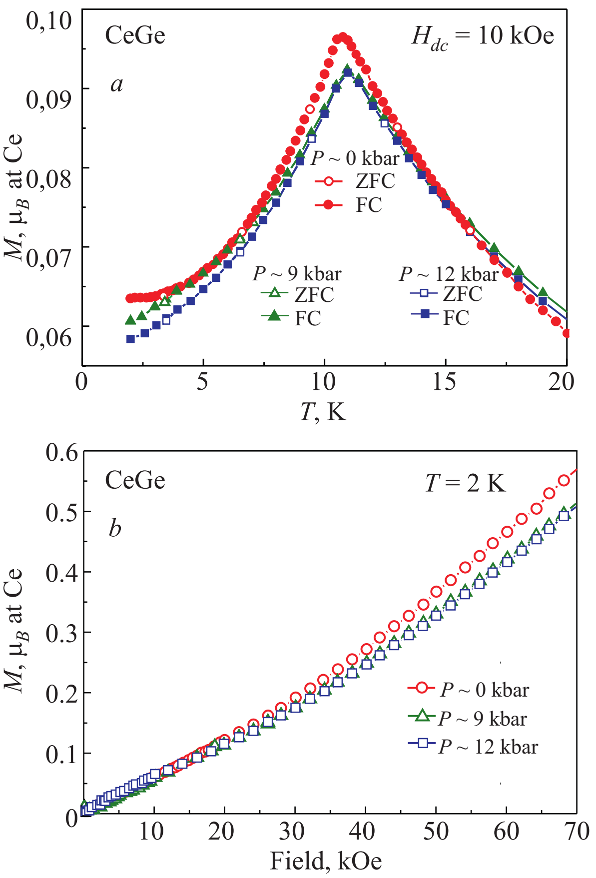

Fig. 1. (Color online) dc susceptibility curve measured for CeGe under an applied magnetic field of 10 kOe up to 12 kbar (*a*). Isothermal magnetization behavior of CeGe under pressure at 2 K. The curvature seen at 20 kOe indicates the onset of the flipping process. Continuous lines drawn are guides to the eye (*b*).

At smaller fields, however, there exists a strong irreversibility in FC and ZFC with at least two different contributions into the ZFC curve and a strong increase of the FC susceptibility below T_N [4]. Such an irreversibility was associated with the existence of a very small ferromagnetic component in the magnetic structure. In order to explore whether there are any effects in the magnetic structure induced by pressure, we display the isothermal magnetization behavior 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. Such a curvature is quite extended in magnetic field, indicating a progressive flipping of the magnetic moments. We observe that this curvature slightly diminishes for $P = 12$ kbar, the highest applied pressure. This suggest that pressure is inducing subtle differences in the magnetic structure.

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. The comparison between the effect of hydrostatic pressure and applied magnetic field will provide information on the nature of the relevant physics.

It is clear from Fig. 2 that applied pressure and magnetic field are not equivalent as tuning parameters. Although both reduce the peak height due to the magnetic superzones, the behavior of the resistivity is quite different in each case. The application of field reduces the resistivity everywhere below T_N and has the most effect on the peak itself. The application of 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 whilst applied field suppresses the peak associated with the magnetic superzones and also suppresses the Néel temperature, the application of pressure actually slightly enhances T_N as well as reducing the height of the peak. The enhancement is small, at ~ 20 mK·kbar^{-1}. T_N is taken to be the point at which the gradient of ρ(T) becomes negative as the temperature is reduced.

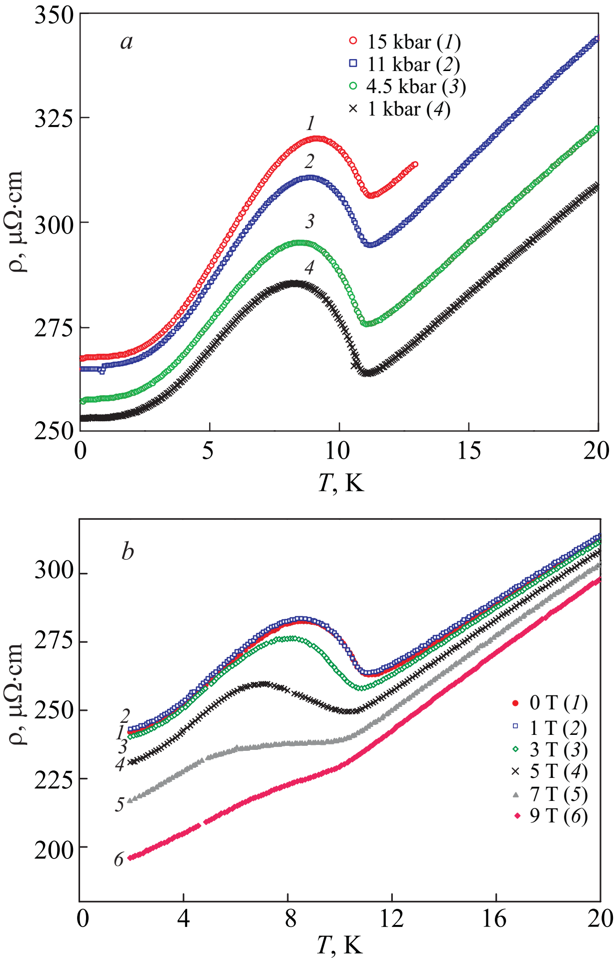

Fig. 2. (Color online) The application of pressure (*a*) can be seen to affect the resistivity in a number of ways: the residual resistivity is raised, the peak height above the curve is suppressed, and the Néel temperature is slightly enhanced. The effect of field is different [6] (*b*). The peak is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

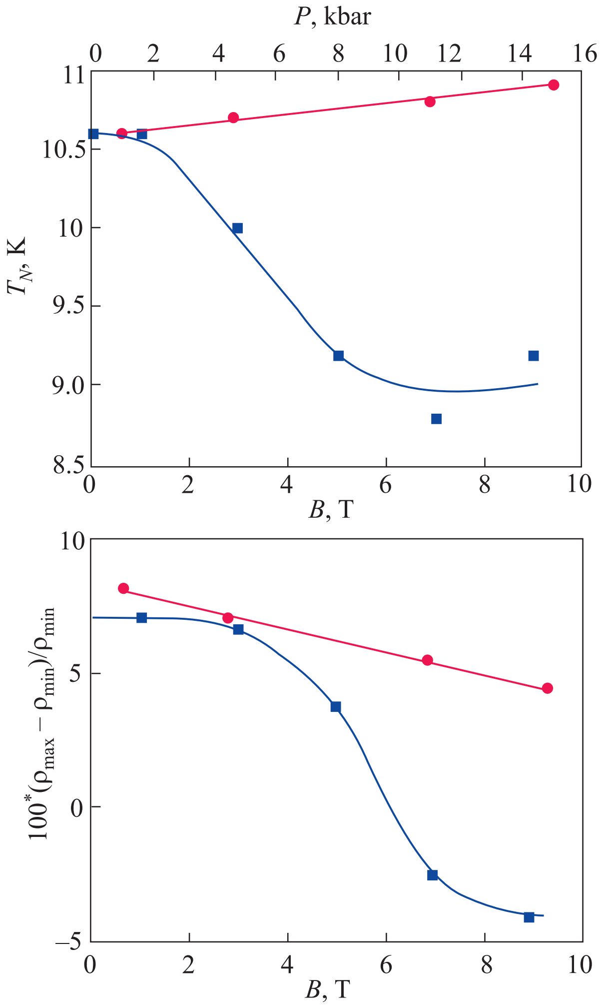

Fig. 3. (Color online) The effects of applied field and pressure on the Néel temperature (*a*) and peak height (*b*). In both plots the red circles (●) correspond to the pressure axis and the blue squares (■) to the applied field.

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

The residual resistivity is enhanced by the application of pressure and reduced with the application of magnetic field (Fig. 5).

The resistivity of a metal is determined by the number of available charge carriers and the total scattering rate of the carriers. The overall scattering rate is a sum of the scattering rates associated with a number of different processes that will in general have different dependencies on temperature, pressure, applied magnetic field, etc.

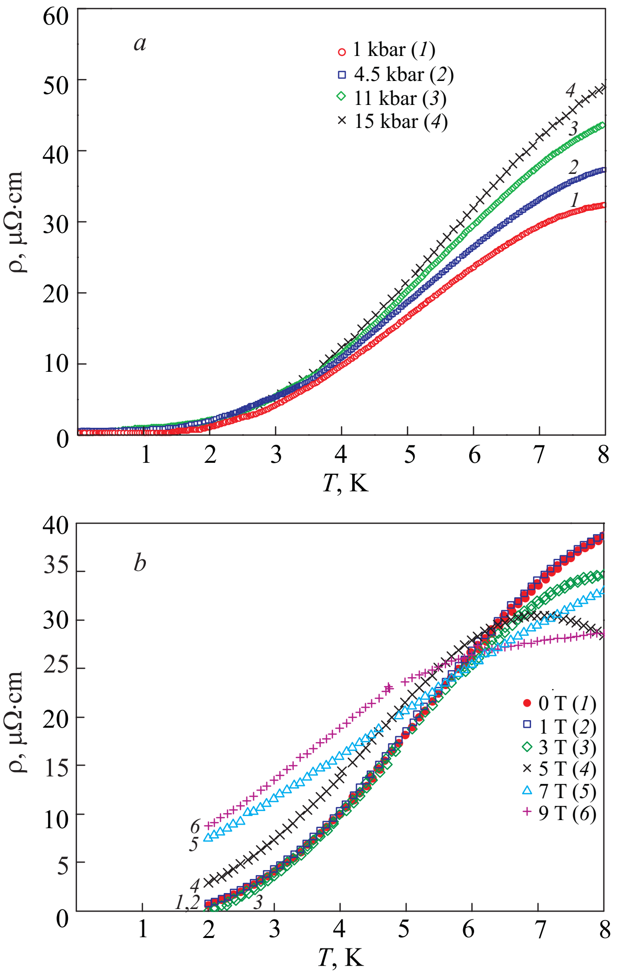

Fig. 4. (Color online) By subtracting the residual resistivity it is easier to see that whilst the application of pressure increases the curvature, applied field changes the behavior of the resistivity more drastically.

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

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

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

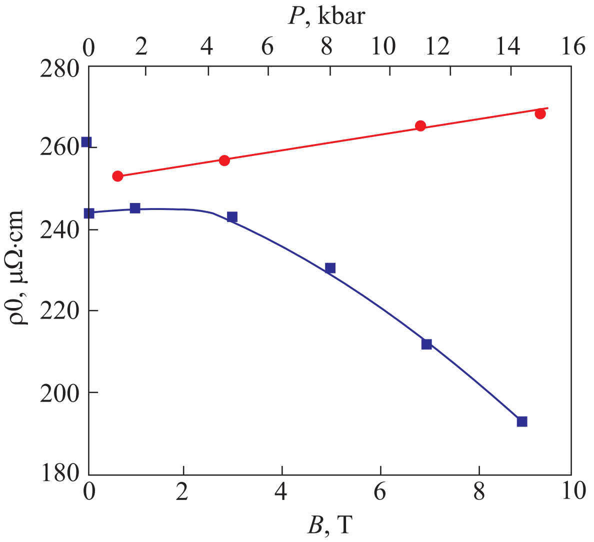

Fig. 5. (Color online) Effect of pressure and field on ρ_0. The red circles (●) correspond to the pressure axis and the blue squares (■) to the applied field.

τ_{em} is the scattering of conduction electrons with the absorption and emission of magnetic excitations. Again these scattering events can be normal or Umklapp processes.

Finally, τ_{Kon} gives the rate of scattering from the partially screened local moments. These local moments are antiferromagnetically coupled to the electron cloud surrounding them and screening the moment by a substantial fraction. This screening gets more complete as the temperature is lowered, leading to resistivity that increases with lowering temperature. 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 as presented by Coqblin *et al.* in Ref. 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 energy scales is one of the fundamental reasons for the interest in the heavy fermion systems. It would be expected that in this situation some relatively small change in any tuning parameter could lead to large changes in the systems properties. Indeed, the application of field does appear to affect a large change in the resistivity of the system. It is possible, in a very simple way, to compare the energy introduced into the system via an increase in temperature, magnetic field and hydrostatic pressure. In useful 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, however, the work done on a test cube with realistic modulus of compression gives the energy as $\sim 9{\cdot}10^{-5}$ eV·kbar^{-1}. The fact that the effect of pressure is markedly less than that of field suggests, therefore, that this approximation is lacking. This is not surprising as this very simple comparison neglects any effects arising from the strongly correlated electrons in the system. A more telling comparison would require a calculation of the lattice spacing dependence of the exchange interaction. Neutron scattering may well be able to reveal this relationship and shed light on the seeming stability of the magnetic state under pressure.

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

3.1. Temperatures greater than the Néel temperature

To understand the effect of pressure on the resistivity of CeGe it is necessary to consider how the applied pressure changes the magnetic interactions in the system. There are two mechanisms to consider: the 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 the localised f electrons and the conduction electrons. In cerium based compounds the pressure effectively squeezes the one f electron out of the localised f orbital and into the conduction band, reducing the contribution that can be made to the local moment to zero eventually. In the intermediate regime, the application of pressure is serving to increase the hybridisation between the f electrons and the charge carriers. This enhances the strength of the Kondo scattering interaction leading to an increased resistivity. This can also provide an explanation for the rising Néel temperature; the enhanced scattering is increasing the entropy of the system making it more favourable for the magnetic ordering to which the system is already prone. It would therefore be reasonable to look for an enhanced magnetic susceptibility. However, this is not observed. The effect of the depletion of the f orbital may well be dominant.

The ratio of $T_K / T_N \sim 0.75$ means that we can place CeGe, under 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 is having no effect on the system in general — it just so happens that the effects on the Néel temperature are cancelled out for the most part in this pressure range. There are many cerium based heavy fermion compounds that 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 of the possible indicators of how close 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, the materials with a very large γ do not order magnetically and are dominated by the Kondo interaction. In CeGe, specific heat measurements have shown $\gamma \sim 260$ mJ·K^2·mol. This is somewhere in the middle of the range that has been observed. Work on $\mathrm{CeSi}_{1-x}\mathrm{Ge}_x$ [5] has shown that the introduction of 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, leading to an effective increase of pressure. As x is increased the Néel temperature is increased from ~ 6–10 K as would be expected if the system was following the standard Doniach picture.

3.2. Temperatures below the Néel temperature

As the temperature is reduced towards T_N and the system is nearing the second order transition to the antiferromagnetic state, the magnetic fluctuations will become increasingly long-lived and long-ranged. When the system orders antiferromagnetically the magnetic fluctuations present above the transition are frozen out. This means a reduction in scattering rates which, if this was the dominant effect, would lead to a reduction in resistivity (see Ref. 8). However, as has been mentioned, this is often not the case and the resistivity increases just below the transition. The Fermi surface is fundamentally changed by the 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 left in 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 behaviour 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 the application of 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 that will then have on the exchange interaction and electron–electron scattering. Likewise, the exact effects of pressure on the lattice parameters and thence on the band structure and the 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 $\mathrm{Sr_2RuO_4}$. The effective interaction, assumed to be magnetic, was then studied at different band filling factors. They showed that even within the relatively simple model explained, the effective interaction could have attractive regions in *k* space. If a Cooper pair can exist which principally samples these regions, then an instability to superconductivity may exist. In this single band it was found that the interaction may be attractive and of 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 the resistivity anomalies in the heavy rare earths (Gd–Tm) given by Elliott and Wedgwood [10] in 1963 is based on the magnetic ordering having 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. The form of the Fermi surface and the symmetry of the crystal play an important role in determining, within this theory, the effect of the magnetic ordering on the electron scattering and hence the resistivity. Calculations done by Ellerby *et al.* in Ref. 11 based on the theory of Elliott and Wedgwood, are successful at explaining the effect of applied magnetic field on the 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 necessary type to make magnetic superzones very important in descriptions of transport, i.e., of 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 show magnetic superzones. CeGe is neither hexagonal, nor has neutron diffraction shown any ferromagnetic component to the magnetisation. Furthermore, 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 neutron study to determine.

4. Conclusions

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

The changes in the form of the resistivity are explained in terms of the various scattering rates and changes to the carrier concentration that are present in a system caught in a fine balancing act between two states with comparable energy scales. The curvature in the isothermal magnetisation associated with the zero-field AFM state is suppressed with the application of pressure. This supports the observation that pressure is altering 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.

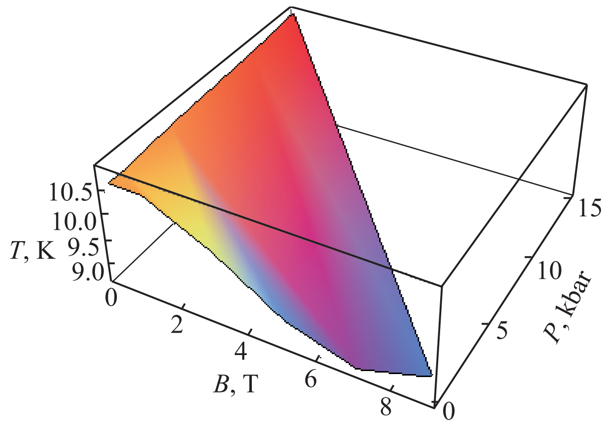

Fig. 6. (Color online) The Néel temperature has been found to be significantly diminished by applied field but only slightly enhanced by the application of pressure. The relationship is that $dT_N/dP \sim \sim 0.02$ K·kbar^{-1}. Whilst this change is only very small, it is comparable to other heavy fermion magnets [12]. The effect of applied pressure on the form of the resistivity is marked. The peak height and residual resistivity are substantially lowered and raised respectively.

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