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Anisotropy of the magnetic and electrical properties of CeSi_x

J Pierre[†], O Laborde[‡], E Houssay[§], A Rouault[§], J P Sénateur[§] and R Madar[§]

[†] Laboratoire Louis Néel, CNRS, BP 166 X, 38042 Grenoble Cédex, France

[‡] Centre de Recherches sur les Très Basses Températures (CRTBT) and Service National des Champs Intenses, CNRS, BP 166 X, 38042 Grenoble Cédex, France

[§] Institut National Polytechnique de Grenoble, Ecole Nationale Supérieure de Physique de Grenoble Unité de Recherche 1109 associé au, CNRS, BP 46, 38402 Saint Martin d'Hères Cédex, France

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Abstract. We report magnetic and resistivity measurements between 2 and 300 K on well characterised CeSi_x single crystals ($x = 1.71$ and 1.86). Both the magnetic and the transport properties of this ferromagnetic dense Kondo system are strongly anisotropic. We compare the resistivity results with those of $\text{NdSi}_{1.7}$ which crystallises with the same structure and exhibits a simpler magnetic behaviour. An anomaly is observed at high temperatures (230 K and 260 K respectively for $x = 1.71$ and $x = 1.86$) in the resistivity of CeSi_x which could result from some structural mechanism.

1. Introduction

Metallic cerium compounds exhibit a large variety of magnetic behaviours from magnetically ordered mixed-valence, heavy-fermion to Kondo lattice systems. These properties are due to the location of the 4f electron of the Ce ion near the Fermi level and to its strong resulting interaction with the conduction electrons. Depending on the relative values of the microscopic parameters (exchange interaction, electronic density of states, etc), different cases can be found. In particular, the system can undergo a transition to a non-magnetic Kondo lattice state at low temperatures. If the RKKY interaction is large enough to stabilise the magnetic moments, order occurs at low temperatures.

Ce–Si compounds near to 1:2 stoichiometry follow this magnetic scheme with the occurrence of Kondo or intermediate-valence properties [1–7]. CeSi_2 is a well known intermediate-valence compound, which does not order at low temperatures. For CeSi_x compounds, the main effect of the silicon deficiency is to reduce the Kondo temperature; a crossover from non-magnetic to magnetic behaviour at low temperature occurs near $\text{CeSi}_{1.83}$. However, there is still evidence for Kondo interactions in $\text{CeSi}_{1.7}$ from specific heat or resistivity data [5]. The crystal-field anisotropy is large in magnetic phases as well as in non-magnetic phases [5].

CeSi_2 crystallises [8] in the tetragonal ThSi_2 structure. The variation in x from a value of 2 leads in a first step to the creation of silicon vacancies without alteration of the structural symmetry. For x smaller than about 1.75 the compounds crystallise in the

orthorhombic GdSi_2 structure. The limit of the homogeneity range is estimated to be about $x = 1.6$. For smaller x , samples are no longer single phase. Although magnetic behaviour is certainly linked to the structure of the compounds, the clear relation between magnetism and structure is not well understood.

Moreover physical properties are strongly anisotropic with respect to the crystallographic orientation [3, 5]. It is then necessary to perform measurements on single crystals of very good quality and which are well characterised. In order to obtain insight into these different questions, we have performed magnetic and resistivity measurements carried out in a large temperature range, on two single crystals of CeSi_x with respective concentrations $x = 1.71$ and 1.86 . We compare the resistivity measurement with those obtained on $\text{NdSi}_{1.7}$ which crystallises in the same structure and which displays a more simple magnetic behaviour than the CeSi_x compounds do.

2. Experimental details

Single crystals of cerium disilicides have been grown by a Czochralski technique in a modified Hukin-type crucible set up previously for the crystal growth of refractory metal disilicides [9]. To summarise briefly this powerful technique, we may recall that the crystals are pulled from an RF-levitated melt while simultaneously a polycrystalline rod of the compound is pushed inside the cold crucible, thereby supplying the melt. Thus the molten volume remains constant and the liquid–solid interface is stabilised. The pulling rate is $2\text{--}3 \text{ mm h}^{-1}$. The synthesis of the polycrystalline rods and the crystallisation are carried out successively by changing only the cold-crucible part of the system. The polycrystalline rods were obtained by RF melting of cerium ingots (purity, 99.9 or 99.99%) and silicon lumps (purity, 99.9999%). The starting compositions were CeSi_2 and $\text{CeSi}_{1.73}$.

For the crystal growth, we used oriented seed cut from a polycrystalline ingot obtained by pulling with a tungsten needle.

The monocrystalline samples for the transport and magnetic measurements were cut along the main crystallographic directions, after orientation by x-ray Laue diffraction. Four samples were cut from the large single crystals with typical dimensions of $1 \text{ mm} \times 1 \text{ mm} \times 5 \text{ mm}$. Their main dimensions are parallel either to the a or to the c crystallographic directions.

The first crystal is tetragonal (ThSi_2 structure type), and the second is orthorhombic (GdSi_2 structure type). The lattice parameters of the samples used for the physical measurements are $a = 4.188 \text{ \AA}$, $c = 13.884 \text{ \AA}$ and $a = 4.192 \text{ \AA}$, $b = 4.119 \text{ \AA}$, $c = 13.911 \text{ \AA}$, respectively. Comparison with our previous work on the variation in the unit-cell parameters as a function of x for CeSi_x homogeneous samples [10] gives the compositions $\text{CeSi}_{1.9}$ and $\text{CeSi}_{1.7}$, respectively.

However, the lattice parameters for both crystals, obtained from powder x-ray diffraction on ground samples, show a slight variation along the crystal. These changes in composition can be related to a continuous slight volatilisation of silicon during the crystal growth process or to some deviation of the liquidus curve for these compositions in the Ce–Si phase diagram.

The densities determined by the Archimedes method on the samples used for the physical measurements are 5.24_5 and 5.20_6 which give the compositions $\text{CeSi}_{1.86}$ and $\text{CeSi}_{1.71}$, in good agreement with the values obtained by x-ray diffraction.

3. Magnetic measurements

The magnetic properties of the samples were measured between 1.5 and 300 K, using a superconducting magnet with fields of up to 7.5 T.

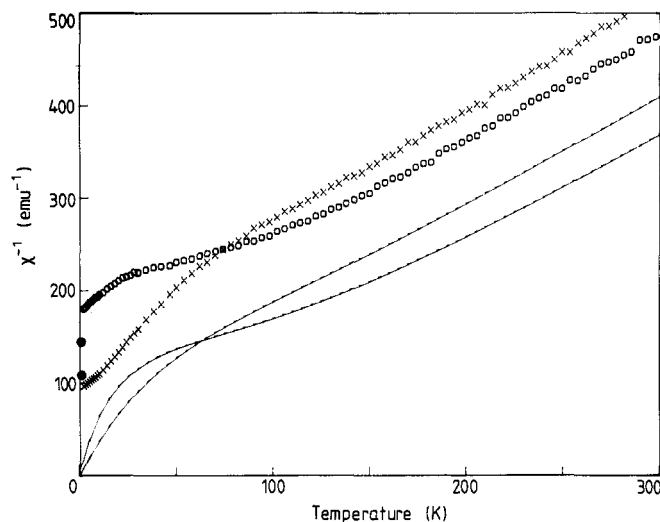


Figure 1. Reciprocal susceptibility for a $CeSi_{1.86}$ single crystal, with the field along the a axis (\times) or c axis (\circ): —, curves calculated with a crystal-field model (see text).

3.1. $CeSi_{1.86}$

The reciprocal susceptibilities of $CeSi_{1.86}$ for a field parallel to the c axis or to the a axis are given in figure 1. The data are very similar to those given in [5] for a sample of the same composition; the compound behaves as a Fermi liquid at low temperatures, and the susceptibility is larger for a field in the basal plane below about 70 K, the sign of the anisotropy changing above this temperature.

Such an anisotropy may be accounted for by the uniaxial crystalline electric field (CEF). CEF parameters have been previously deduced from the susceptibility variation [3, 5].

Inelastic neutron scattering experiments have also been performed on this compound as well as on the stoichiometric $CeSi_2$ compound [11]. A strong phonon scattering occurs for these compounds as well as for $LaSi_2$ compound. $LaSi_2$ exhibits phonon features between 12 and 40 meV [11], but the intensities of phonon lines are not the same as for $CeSi_2$. Thus the phonon spectrum has been evaluated for Ce compounds using the wavevector dependence of the neutron cross section and subtracted in order to obtain the magnetic cross-section.

For $CeSi_2$, two broad magnetic excitations were found at 30 and 50 meV, corresponding to an overall CEF splitting of about 580 K. For $CeSi_{1.86}$, a broad magnetic inelastic spectrum occurs between 20 and 30 meV, which confirms the occurrence of excited levels in this energy range. However, contrary to the case of $CeSi_2$, it is not possible to separate the two inelastic transitions. This may be explained not only by the occurrence of two closely spaced excitations but also by a smearing of excitations due to different CEF level schemes on various sites, depending in turn on the distribution of Si vacancies. The overall CEF splitting is smaller for $CeSi_{1.86}$ than for $CeSi_2$.

A quasi-elastic scattering also appears for these compounds, the width of which increases with increasing temperature [11, 12]. From the residual width observed at low temperatures for $CeSi_{1.86}$ (about 1.7 meV), we may deduce a Kondo temperature of 20 K, whereas the residual linewidth for $CeSi_2$ was found to be 3.5 meV, corresponding to a Kondo temperature of about 40 K. These values are slightly smaller than those deduced previously from other data [2].

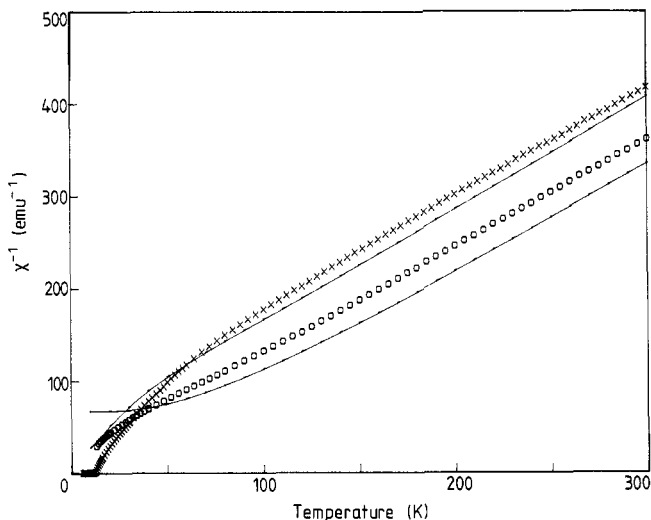


Figure 2. Reciprocal susceptibility for a $\text{CeSi}_{1.71}$ single crystal with the field along the a axis (\times) or the c axis (\circ); —, crystal-field calculations (see text).

A crude representation of the anisotropy in a crystal-field-only model may be obtained using the set of CEF parameters: $B_2^0 = -4.5$ K, $B_4^0 = 0.9$ K and $B_4^4 = 4.5$ K (full curves in figure 1). These values are very close to the parameters given in [5] and lead to energies of excited levels of 290 and 340 K, in qualitative agreement with neutron data.

The real susceptibility of the compound is much smaller than deduced from the CEF-only model, owing to the Kondo screening. However, tentative attempts to match the real susceptibility of the compound by shifting the theoretical crystal-field model curves as a whole [5] are clearly wrong; it would lead for example to a finite paramagnetic moment at low temperatures, whereas the real susceptibility turns out to be constant.

No general theory which could give a complete description of the susceptibility curve in the presence of a crystal field and the Kondo effect is available at present. However, the theory in [13] gives a good description at $T = 0$ K. Using this theory, the CEF parameters in [5] and the value of the Kondo temperature (20 K) as deduced from [11], we obtain a correct order of magnitude for the susceptibilities at 0 K (full circles in figure 1). The calculated anisotropy is, however, smaller than the observed value; thus the crystal field is certainly underestimated. The Kondo effect indeed tends to mix the initial CEF wavefunctions and thus to reduce the anisotropy.

3.2. $\text{CeSi}_{1.71}$

Magnetic measurements were performed on two different crystals from the same batch, with identical results (figure 2). In agreement with previous data [5], this compound turns out to be ferromagnetic at $T_c = 12.5$ K. The magnetic moment is aligned in the basal plane, and the spontaneous magnetisation reaches $0.47\mu_B$ at 1.5 K (figures 3 and 4). No significant spontaneous magnetic component (less than $0.015\mu_B$) is observed for a field along the c axis, which proves the good quality and orientation of the sample. In addition, we do not observe any 'step' in the magnetisation curve for a field in the basal plane, contrary to the results in [4] for a $\text{CeSi}_{1.70}$ sample. No evidence for the occurrence of any antiferromagnetic component can be obtained from the present magnetisation data.

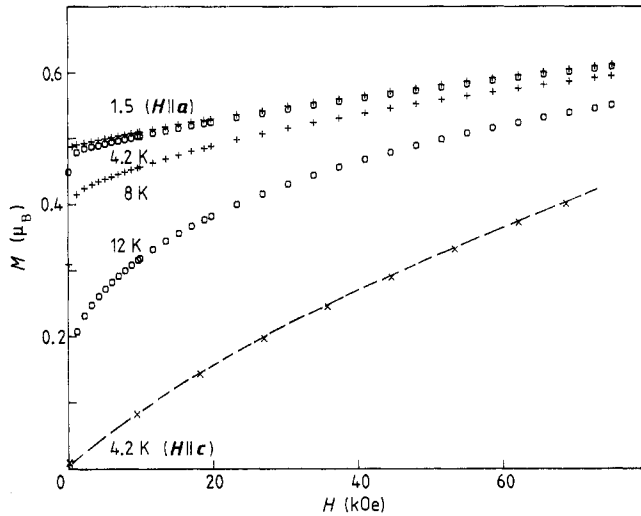


Figure 3. Magnetisation curves for $CeSi_{1.71}$ for H along the a axis. The magnetisation at 4.2 K along the c axis is also given.

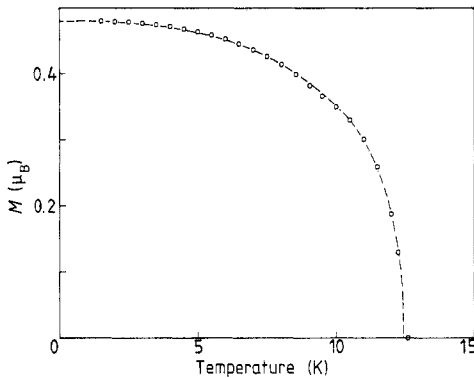


Figure 4. Spontaneous magnetisation for $CeSi_{1.71}$ as a function of temperature.

In the paramagnetic range, the susceptibility is larger in the basal plane below 30 K, whereas it is smaller above this temperature (figures 3 and 4) and the anisotropy reaches 14% at room temperature, which is slightly larger than found in previous measurements [3, 5] for $CeSi_{1.70}$.

For this compound, the Kondo temperature is smaller than for $CeSi_{1.86}$ and can be estimated to be of the order of 10 K [4]. Thus we describe in a first step the magnetic properties within a pure CEF model. Our best fit of the data is with the CEF parameters $B_2^0 = -7.0$ K, $B_4^0 = 0.5$ K and $B_4^4 = 2.5$ K. The larger value of the B_2^0 -term compared with that obtained in [5] is related to our larger anisotropy at high temperatures. The overall susceptibilities (full curves in figure 2) are calculated to be larger than observed at high temperatures, which may be related to the Kondo interaction, whereas they are found to be smaller at low temperatures owing to the ferromagnetic interactions.

Using the preceding CEF parameters and a value of the molecular-field parameter obtained from the ordering temperature, we obtain a theoretical value for the magnitude of the saturation moment ($0.88\mu_B$) for this compound in the pure CEF model, and it should be aligned in the basal (a, b) plane. The predicted direction of the moments

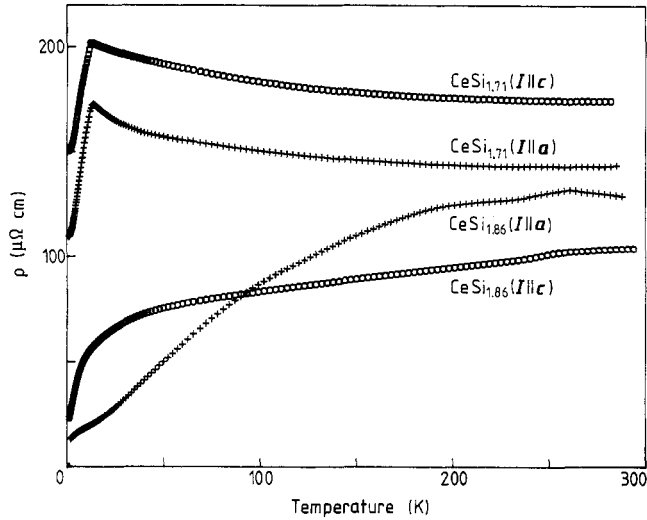


Figure 5. Resistivities of $\text{CeSi}_{1.71}$ and $\text{CeSi}_{1.86}$ single crystals. For both concentrations the current is along the a or c axis.

agrees with experiment, but the discrepancy in the magnitude is attributed to the reduction by the Kondo effect. Within the theory of [13], we reproduce the saturation moment of $0.47 \mu_B$ by introducing a Kondo temperature of 10 K, in good agreement with previous determinations from other data [2].

4. Resistivity measurements

The resistivity was measured on the same samples between 1.5 K and room temperature by a four-probe method and a conventional AC technique. Electrical contacts were mechanically pressed on the sample.

The resistivities are plotted against T for both silicon concentrations and for $I \parallel a$ and $I \parallel c$ in figure 5. The main features previously reported for these compounds [3, 5] are displayed by the data; $\rho(T)$ curves are strongly different for $\text{CeSi}_{1.71}$ which orders at low T and for $\text{CeSi}_{1.86}$ which does not. For $x = 1.71$ a well defined maximum appears at the ordering temperature; this is followed just below the ordering temperature by a sharp decrease in ρ . For $x = 1.86$, the thermal variation is smooth from high to low temperatures. A particularly strong anisotropy is observed for $\text{CeSi}_{1.86}$ between the two current directions. The values of the residual resistivity $\rho(T = 0)$ are very different for the two concentrations. They are larger than $100 \mu\Omega \text{ cm}$ for $\text{CeSi}_{1.71}$ and are only a few tens of microhm centimetres for $\text{CeSi}_{1.86}$.

New features for the resistivity can also be seen in the results.

4.1. $\text{CeSi}_{1.86}$

At variance with the measurements in [3] the resistivity of $\text{CeSi}_{1.86}$ exhibits an anisotropic behaviour at room temperature, with a crossing of the two curves at around 100 K, and a sign reversal of the anisotropy below. The absolute value of ρ is only known with an accuracy of about 10% because of the uncertainty in the geometrical form factor. The anisotropy effect at high temperatures is as yet beyond the uncertainty, and the change

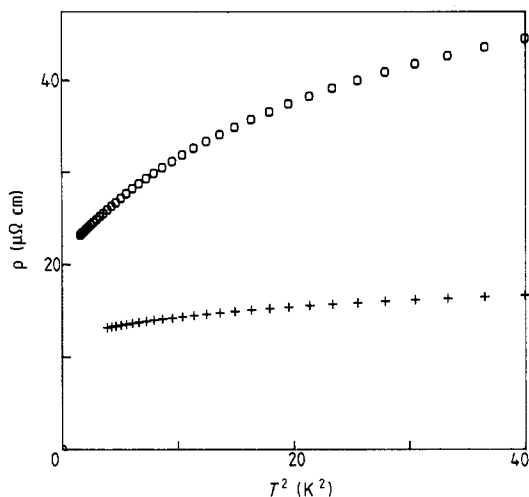


Figure 6. Resistivity of $CeSi_{1.86}$ against T^2 , with the current along the a axis (+) or the c axis (○).

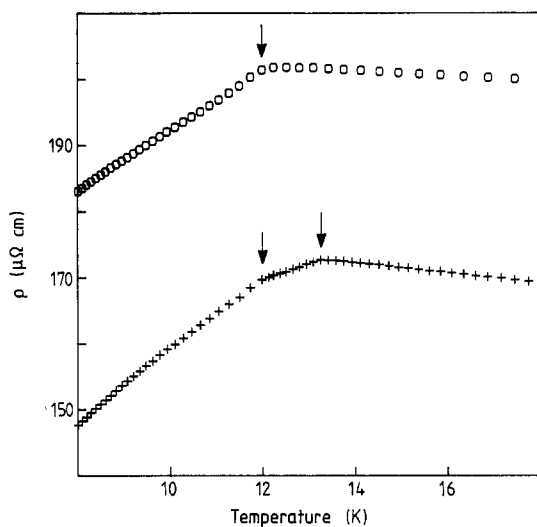


Figure 7. Resistivity of $CeSi_{1.71}$ near the ordering temperature. The current is along the a axis (+) or the c axis (○).

in sign of the anisotropy is very similar to the behaviour of the magnetic susceptibility. Close examination of the data at low T shows that the T^2 law reported in [3] is not obeyed in a wide temperature range. A plot of ρ against T^2 (figure 6) indeed displays continuous curvature. This result can be seen in our data and not in those of [3] as a consequence of the larger precision achieved in our resistivity measurements. The curvature apparent in figure 6 could be accounted for by a T^n law with $1 < n < 2$ but only in too small a temperature range to give real significance to that power law.

4.2. $CeSi_{1.71}$

For the resistivity of $CeSi_{1.71}$ we again observe a larger anisotropy at room temperature than in [5]. The maxima at the ordering temperature also exhibit a more complex structure. For I along the a axis, a plot of ρ against T shows two well defined anomalies at 12 and 13.3 K (figure 7) while, for $I \parallel c$, only one anomaly clearly appears at 12 K. These anomalies are clearly beyond the uncertainty of our measurements. We can also

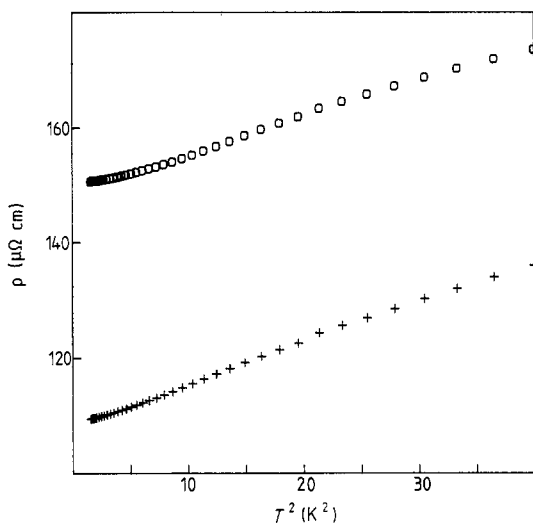


Figure 8. Resistivity of $\text{CeSi}_{1.71}$ against T^2 , with the current along the a axis (+) or the c axis (○).

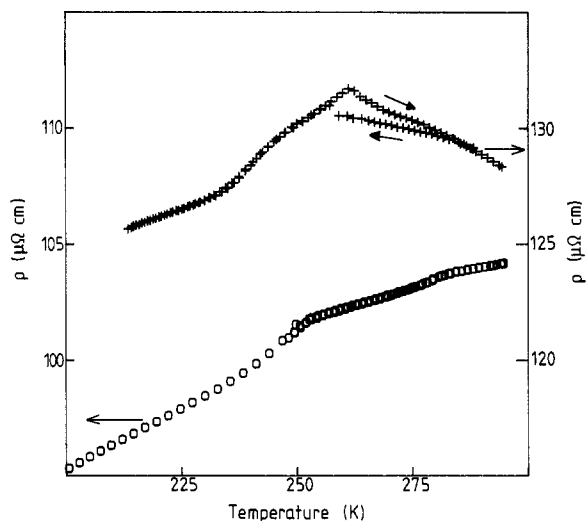


Figure 9. Resistivity of $\text{CeSi}_{1.86}$ near the high-temperature anomaly for increasing and decreasing T , with the current along the a axis (+) or the c axis (○).

expect another anomaly at 13.3 K for $I \parallel c$ but with a change in the slope of the curve of ρ against T too small to be detected. This double transition seems very similar to that reported in the specific heat for some single crystals [5]. We have no explanation at the moment for these anomalies. We also note that the low-temperature variations in ρ are rather different from those of the $\text{CeSi}_{1.86}$ compound. The results are shown in figure 8 for comparison.

4.3. High-temperature anomalies

We can see in figure 5 that a cusp appears at high temperatures especially in $\text{CeSi}_{1.86}$ when the current flows along a . The details of $\rho(T)$ in that domain of temperatures are shown in figures 9 and 10. Anomalous behaviour is found for all the curves except that for $\text{CeSi}_{1.71}$ with $I \parallel c$. Hysteresis is detected on cooling and warming cycles for both concentrations for $I \parallel a$. The transition is located near 260 K for $\text{CeSi}_{1.86}$ and 230 K for $\text{CeSi}_{1.71}$. Hysteresis cycles spread over several kelvins.

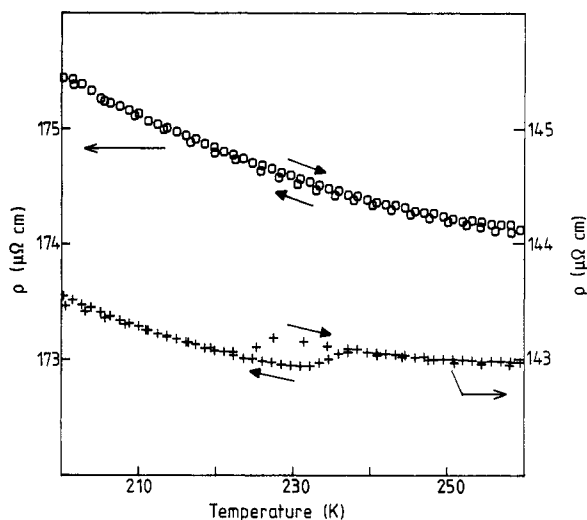


Figure 10. Resistivity of $CeSi_{1.71}$ near the high-temperature anomaly for increasing and decreasing T , with the current along the a axis (+) or the c axis (O).

5. Discussion

Strong anisotropy is the main feature of the magnetic behaviour of the $CeSi_x$ compounds. $CeSi_{1.86}$ exhibits the largest magnetic susceptibility at low T for H parallel to (a, b) . This plane is also an easy-magnetisation plane for $CeSi_{1.71}$; the moments order ferromagnetically in the plane. Ferromagnetic correlations occur in that sample above T_c and also in the other sample which does not order but which undergoes a transition to a Kondo lattice state at low temperatures. A trend to Kondo behaviour is however, found in the magnetically ordered system. This leads in particular to a strong reduction in the magnetic moment carried by the cerium ion. Moreover, crystal-field effects complicate the analysis of the experimental results at high temperatures.

The magnetic behaviour is strongly reflected in the resistivity measurements. In particular the anisotropy with respect to the crystallographic orientation of the sample is clearly in evidence. A complex magnetic behaviour is apparent for instance in the deviation from the simple T^2 variation at low temperatures found for $CeSi_{1.86}$. Such a T^2 law should be expected for the resistivity of a Kondo lattice.

The splitting of the magnetic transition observed for $\rho(T)$ in $CeSi_{1.71}$ is not well understood. It could result from two different magnetic structures in the different temperature domains or it could be due to strong correlations between the moments in the plane followed at lower temperatures by complete ordering of the whole moments. We note that magnetic measurements are not carried out in the range of T involved with enough precision to observe the intermediate phase. Moreover the magnetic field required for these measurements could hide this effect. The agreement between the two determinations of T_N from magnetic and resistive measurements is, however, quite good.

A fraction of the resistivity anisotropy could lay in the anisotropy of the carrier parameters, and in particular of the Fermi surface. At high temperatures, crystal-field effects could play a part in the resistivity variation. As calculations of these effects are not available and are beyond the scope of this work, in order to estimate their influence on $\rho(T)$ we shall compare the measurements for $CeSi_x$ with results for a similar compound $NdSi_{1.7}$.

We have also performed experiments on $NdSi_{1.7}$ single crystals; it crystallises with the same orthorhombic structure as $CeSi_{1.71}$ and orders ferromagnetically at 10 K [14].

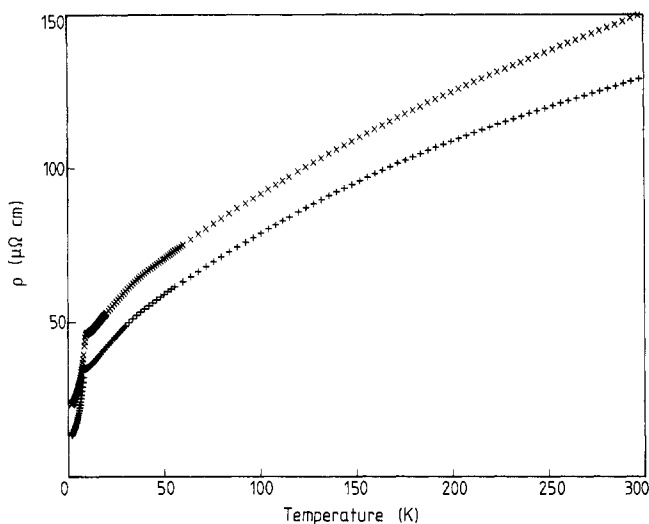


Figure 11. Resistivity of $\text{NdSi}_{1.7}$ with the current along the a axis (+) or the c axis (x).

The spontaneous magnetisation also lies along the a axis and reaches $1.4\mu_{\text{B}}$ at 1.5 K. Two crystals were cut from the same batch, which allowed us to measure the resistivity with the current along the a and c axes. The results are given in figure 11. Apart from a small difference in the residual value, the resistivity thermal dependence is found to be isotropic up to about 40 K. Above this temperature, the slope of ρ against T is larger for $I \parallel c$. Preliminary neutron inelastic scattering experiments show that the crystal-field splitting is about 150 K for this compound. Thus the slope at high temperatures must be ascribed to the phonon scattering term only. The mean phonon contribution is estimated to about $60 \mu\Omega \text{ cm}$ at room temperature, the difference in slope being 20%. We may then infer that this anisotropy is related to the anisotropy of the Fermi surface, which should be checked on La compounds as soon as good crystals become available. Conversely, the magnetic scattering term is roughly isotropic for this compound: $\rho(T_{\text{N}}) - \rho(0) \approx 25 \mu\Omega \text{ cm}$.

For the $\text{CeSi}_{1.71}$ compound, the corresponding term $\rho(T_{\text{N}}) - \rho(0)$ is about twice (about $50 \mu\Omega \text{ cm}$) the value for $\text{NdSi}_{1.7}$, whereas the value of the magnetic moment is much less ($0.47\mu_{\text{B}}$ compared with $1.4\mu_{\text{B}}$). This increase in magnetic scattering together with the larger Curie temperature for $\text{CeSi}_{1.71}$ must be related to a larger 4f-conduction band coupling term, indicating the persistence of Kondo interactions for Ce compounds with this composition. For the $\text{CeSi}_{1.86}$ compound, the large anisotropy in resistivity obviously results from the hybridisation mechanism.

The high-temperature anomalies observed here for single crystals could be linked to the anomalous resistivity behaviour reported for a polycrystalline sample near $x = 1.855$ [15]. This latter is ascribed to crack formation on cooling resulting from a very different variation in the thermal coefficients of expansion along the a and c axes. We note that in our case the concentrations are far away from this critical concentration, that differential dilatation would not affect single crystals and as in the results of [15] that no crystallographic transitions have been detected in our samples in the corresponding temperature domain. Further investigations are in progress but it seems that some subtle structural mechanisms must be invoked to explain the resistive anomalies [16].

Acknowledgment

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