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Unusual elastic behaviour of normal state UPt_3*

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Abstract

A short overview is given of some exceptional low temperature properties of the intermetallic 5f system UPt_3. These properties point to strong renormalization effects leading to heavy fermions, but owing to their temperature dependence, do not give much evidence for a mechanism based on the Kondo model as commonly suggested. Here we report on extensive ultrasonic studies of the heavy fermion state and of the elastic behaviour at higher temperatures. In particular, investigations below room temperature clearly indicate a first-order phase transition in UPt_3 just above the low temperature range where heavy fermion behaviour sets in.

1. Introduction

The hexagonal compound UPt_3 (DO_{19} structure) belongs to the so-called heavy fermion (HF) class of metals [1], which is characterized by extremely large values of both the Sommerfeld coefficient $\gamma = C(T)/T$ of the specific heat and the paramagnetic susceptibility $\chi(T)$ attained at low temperatures. These highly enhanced thermodynamic properties are interpreted as being due to fermionic quasi-particles bearing a very large effective mass $m^* = (100\text{–}1000)m_{fe}$. Upon raising the temperature, the HF state is more or less rapidly left and the parameters of the system adopt "normal" values at higher temperatures. In general no pronounced transition behaviour is observed. Thus the cross-over from the "normal" state at higher temperatures to the HF state only crudely defines a "coherence temperature" T^* of the order of 10 K. Below this temperature the excitations begin to look like fermionic quasi-particles. Since one is dealing with highly correlated electron systems incorporating strong magnetic interactions, the unexpected discovery of superconducting ground states in some of these systems has led to one of the most exciting topics in the rapidly developing field of HF research [2–4].

Showing a superconducting transition at $T_c \approx 0.5$ K, UPt_3 belongs to the subgroup of HF superconductors and possesses a rich variety of anomalous superconducting properties, including a non-exponential temperature dependence of the gap parameter and the existence of several anisotropic superconducting phases, which both give much evidence for an unconventional pairing mechanism and a non-BCS (Bardeen–Cooper–Schrieffer) ground state. In particular, ultrasonic investigations have been very successful in discovering the exotic superconducting properties of UPt_3 [5–8] during recent years and have yielded a lot of information about its superconducting ground state, which nevertheless is not yet well understood. Although the fascinating field of HF superconductivity is a particular challenge for theoretical understanding and gives rise to a high scientific activity, the normal conducting properties of HF systems are no less attractive, because especially the "formation" of the HF state and its origin remain essentially open problems still [3, 9].

In particular, UPt_3 shows a temperature-dependent behaviour when entering the HF state which is in some respects quite different from that observed in other HF systems. This, however, seems to be incompatible with the current idea of a uniform mechanism giving rise to strongly renormalized properties of these systems at low temperatures. The peculiar behaviour of UPt_3 is therefore of considerable importance for giving an adequate description of heavy fermions in general and is intimately related with the main topic of this contribution. Furthermore, the following discussion is enriched essentially by quite new and unexpected results obtained ultrasonically [10], which for the first time clearly indicate a structural transformation of the UPt_3 lattice below room temperature.

2. The Kondo model

A qualitative starting point for thinking about heavy fermions seems to be generally provided by the Kondo effect. All known HF compounds contain at least one atom type with a partially filled f-shell, mostly Ce or

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U, and at least one atom type with no partially filled f-shell, such as Be, Cu, Pt, Pb, etc. At higher temperatures the f-electrons behave magnetically like local moments. Accordingly, the magnetic susceptibility follows a Curie–Weiss law over some hundred kelvins with an effective moment of typically about 3 μ_B before it becomes Fermi liquid like and tends to saturate for $T \leqslant T^*$, pointing to a strongly enhanced Pauli susceptibility. This observation suggests an interaction mechanism whereby the spin entropy of the highly correlated f-electrons is transferred smoothly to the itinerant conduction electrons via hybridization so that the local moments become "compensated" as $T \rightarrow 0$. This scenario is obviously reminiscent of the behaviour found in dilute Kondo systems [11], where a non-magnetic ground state is favoured for excitation energies lower than a characteristic energy of about $k_B T_K$. Here T_K denotes the so-called Kondo temperature and roughly defines the formation energy required for the local magnetic moments to be screened independently by the spin polarization of the surrounding conduction electrons. Since this screening mechanism is a true many-body effect, it is also reflected by the formation of a narrow scattering resonance in the density of states (DOS) near the Fermi energy E_F [12], usually called Abrikosov–Suhl resonance (ASR). Many of the low temperature properties of dilute magnetic systems can be easily understood as a consequence of this very narrow resonance structure in the DOS with a mean halfwidth of the order of $k_B T_K$.

Remarkable similarities in the behaviour of many HF systems to that of solid solutions consisting of magnetic impurities in non-magnetic hosts favoured the idea to characterize them loosely as Kondo lattices. In fact, the properties of HF systems show in many respects Kondoesque behaviour, *e.g.* in many of them one finds the very familiar "Kondo minimum" in the temperature-dependent resistivity $\rho(T)$. This precedes a more or less pronounced maximum at lower temperatures followed by a rapid decrease for $T \rightarrow 0$. The temperature of the resistivity maximum obtained experimentally is often identified with the coherence temperature T^*. This is somewhat lower than T_K and denotes the temperature below which the single-impurity response is modified and coherence effects start to dominate.

Since T_K depends exponentially on the hybridization strength of the f- and conduction electrons, it is very sensitive to changes in the interatomic distances and the lattice constant. Consequently the electronic properties are very pressure dependent and the quasi-particles are strongly coupled to phonons. The volume dependence of T_K is the basis of the so-called Kondo collapse mechanism [13], *i.e.* the system (lattice) becomes potentially unstable with respect to volume contraction by enhancing the hybridization strength. Therefore an enhanced compressibility can be expected when approaching the Kondo regime. In many HF systems a softening of the bulk modulus (inverse compressibility) is indeed observed at lower temperatures and often amounts to 1% or more of the total bulk modulus [14]. This phenomenon can also be explained qualitatively by the formation of an ASR near the Fermi level. Since in the free-electron model the electronic contribution c_B to the bulk modulus is simply $c_B \propto 1/N(E_F)$, it is therefore directly related to the DOS $N(E_F)$. Assuming, furthermore, the validity of Luttinger's sum rule [15], the softening of c_B then essentially reflects the renormalization effects near the Fermi level. This simple view, however, is only justified as long as the symmetry of the system is not altered; it becomes questionable for UPt_3, in particular with regard to the experimental results obtained recently and presented in Section 4.

3. Heavy Fermions in UPt_3

Concerning the normal conducting state at low temperatures, with a high Sommerfeld coefficient $\gamma = 0.42$ J mol^{-1} K^{-2} and a Wilson ratio $\chi(0)/\gamma \approx 0.5$, which seems to be of the typical size for many HF systems, as well as the Curie–Weiss behaviour of the magnetic susceptibility for temperatures higher than about 20 K, UPt_3 shows what is common to all HF systems [1, 16, 17]. However, many features characterizing the cross-over from the high temperature state to the HF state and giving considerable evidence for the above-mentioned model are missing! For example, the temperature-dependent resistivity of UPt_3 does not exhibit any Kondo-type anomalies with a negative temperature coefficient over a certain temperature interval. Instead of this a non-linear but purely metallic-like behaviour quite similar to that of many A15 compounds is found. Furthermore, the characteristic softening of the bulk modulus as $T \rightarrow 0$, confirmed experimentally for several HF systems [14], is obviously absent. As shown in Fig. 1, the steep increase in each of the longitudinal stiffness coefficients accompanied by a non-saturating magnetic susceptibility below 20 K indicates a quite different behaviour of UPt_3 at lower temperatures.

On the other hand, a "resonance" in the DOS near E_F giving rise to strongly renormalized thermodynamic properties can be nicely portrayed by means of ultrasonic attenuation measurements [18, 19]. Its detection with ultrasonic is favoured in particular by the strongly enhanced Grüneisen coupling [20] in UPt_3 which originates in the high electronic Grüneisen parameter $\Omega_\Gamma \approx 10^2$ for volume-changing strain fields of symmetry Γ. Consequently the fermionic quasi-particles at the Fermi level are strongly coupled to longitudinal sound waves and give rise to an electronic contribution to

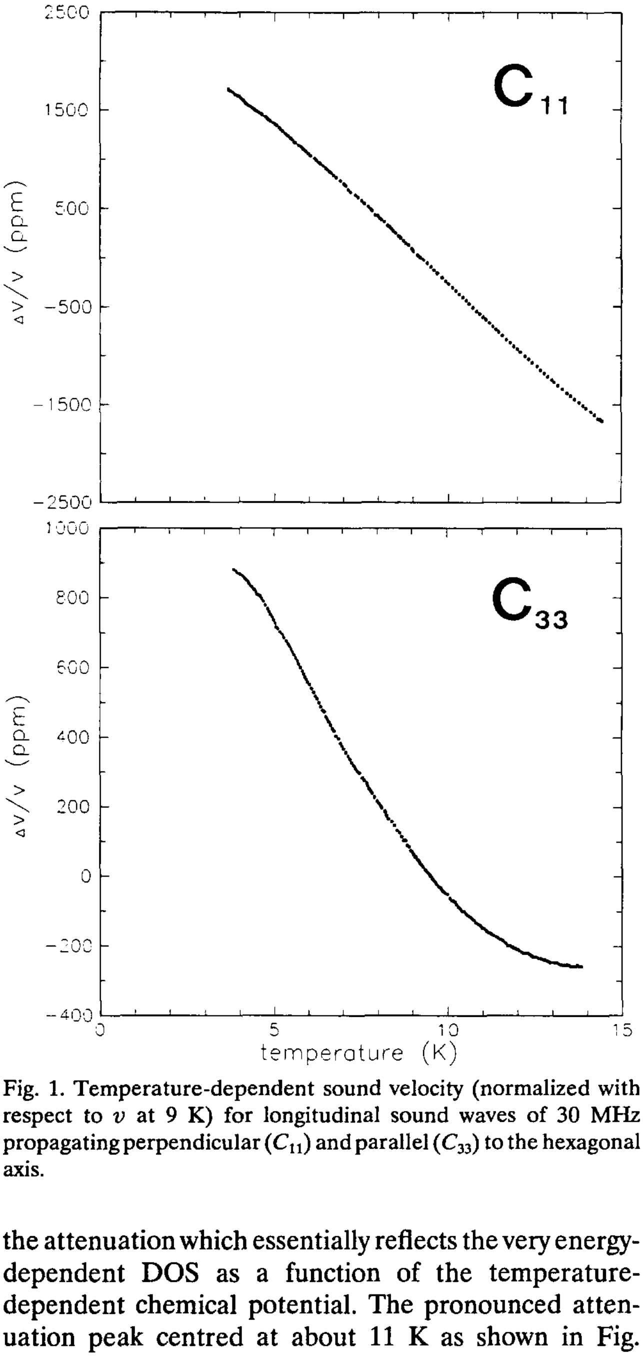

Fig. 1. Temperature-dependent sound velocity (normalized with respect to v at 9 K) for longitudinal sound waves of 30 MHz propagating perpendicular (C_{11}) and parallel (C_{33}) to the hexagonal axis.

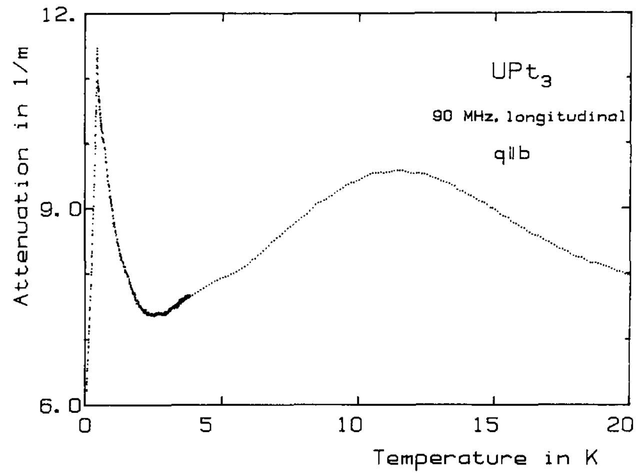

Fig. 2. Temperature dependence of ultrasonic attenuation for longitudinal sound of 90 MHz below 20 K. At 0.5 K the sample becomes superconducting, giving rise to a strong decrease in the electronic contribution.

the attenuation which essentially reflects the very energy-dependent DOS as a function of the temperature-dependent chemical potential. The pronounced attenuation peak centred at about 11 K as shown in Fig. 2 can therefore be directly attributed to the narrow quasi-particle resonance formed. Assuming a lorentzian shape with respect to energy, a mean "resonance width" of about 2 meV is obtained [21], which accounts for the energy scale dominating the low temperature state of UPt_3 and is typical for HF systems in general. The peak position is stable with respect to temperature and does not depend on the sound frequency ω excited (up to 1 GHz), because this contribution to the ultrasonic attenuation mainly refers to the ground state properties of the system. Moreover, the damping amplitude scales with ω^2 over the whole peak width. Hence this attenuation feature cannot be attributed to time-dependent stress relaxation phenomena due to any thermally activated processes.

According to these ultrasonic results, the HF state should be fully developed in UPt_3 for temperatures lower than about 10 K. The appearance of a coherent state is furthermore clearly displayed by a steep decrease in the electrical resistivity ρ exceeding a ratio $\rho(10\ \text{K})/\rho(T_c \approx 0.5\ \text{K}) \approx 100$. Below about 5 K the temperature dependence tends to follow $\rho(T) = \rho_0 + AT^2$ and resembles typical Fermi liquid behaviour with a rather large coefficient $A \approx 0.5\ \mu\Omega\ \text{cm K}^{-2}$ indicative of a strongly enhanced electron–electron interaction [17]. Upon cooling, the decreasing resistivity also gives rise to a pronounced increase in the ultrasonic attenuation due to higher electronic dissipation losses for both longitudinal and transverse sound waves. This very familiar phenomenon known from ordinary metals is dominant in UPt_3 at low temperatures and can also be seen in Fig. 2.

On applying an external magnetic field of strength B, the electronic part of the attenuation is markedly influenced by the Lorentz forces occurring. Apart from the Fermi surface topology, this additional field-dependent contribution mainly depends on the sound wavenumber q and the mean free path l of the quasi-particles, but reduces to the so-called Alpher–Rubin attenuation αB^2 in the limit $ql \ll 1$ [22]. It is remarkable that such behaviour becomes increasingly pronounced in UPt_3 for temperatures even below 100 mK and magnetic field strengths up to more than 10 T (see also Fig. 3). From the attenuation data obtained one can estimate [23] that the mean free path l should not much exceed 1000 Å, although $\rho(T)$ does not saturate even at the lowest temperatures and l is obviously not defect limited.

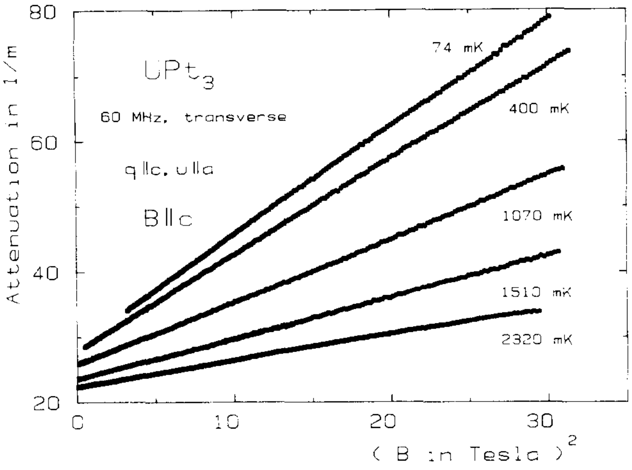

Fig. 3. Field-dependent ultrasonic attenuation (60 MHz) at temperatures well below the coherence temperature $T^* \approx 10$ K *vs.* magnetic field strength squared.

The field-dependent attenuation also follows a B^2 law at higher temperatures, say at 10 K or above. In contrast with the attenuation, the elastic moduli show only minor if any field-dependent changes in this temperature range, constantly demonstrating a high stability of the coherent state formed. This very weak field-dependent behaviour, however, is surprising in so far as it can hardly be understood within the framework of the Kondo mechanism proposed, because the formation of the singlet ground state should indeed be markedly influenced by external magnetic fields [24–26].

Unlike the pronounced stiffening of the bulk modulus at lower temperatures as indicated by longitudinal sound velocity measurements, volume-conserving transverse sound behaves quite differently. For both the C_{44} and C_{66} modes a marked decrease is observed upon cooling below a certain temperature (C_{44}, about 8 K; C_{66}, about 15 K) as shown in Fig. 4. This softening in the overall shear coupling coincides more or less with the formation of the HF state and might simply be interpreted as a weakening of electronic bonds due to a shorter screening length, which is proportional to $1/[N(E_F)]^{1/2}$ in the Thomas–Fermi approximation. On the other hand, this idea is obviously not quite conclusive with regard to the simultaneous stiffening observed for longitudinal strains. Hence it is very probable that electron transfer processes are heavily involved, pointing to an anisotropic character of the HF resonance in the DOS.

Briefly summarizing, we would like to point out that although the existence of a heavy quasi-particle band leading to a pronounced Fermi liquid behaviour at low temperatures is reminiscent of other HF systems, concerning the question of how this state is developed, UPt_3 hardly fits into the generally proposed scheme of the Kondo mechanism owing to singlet formation.

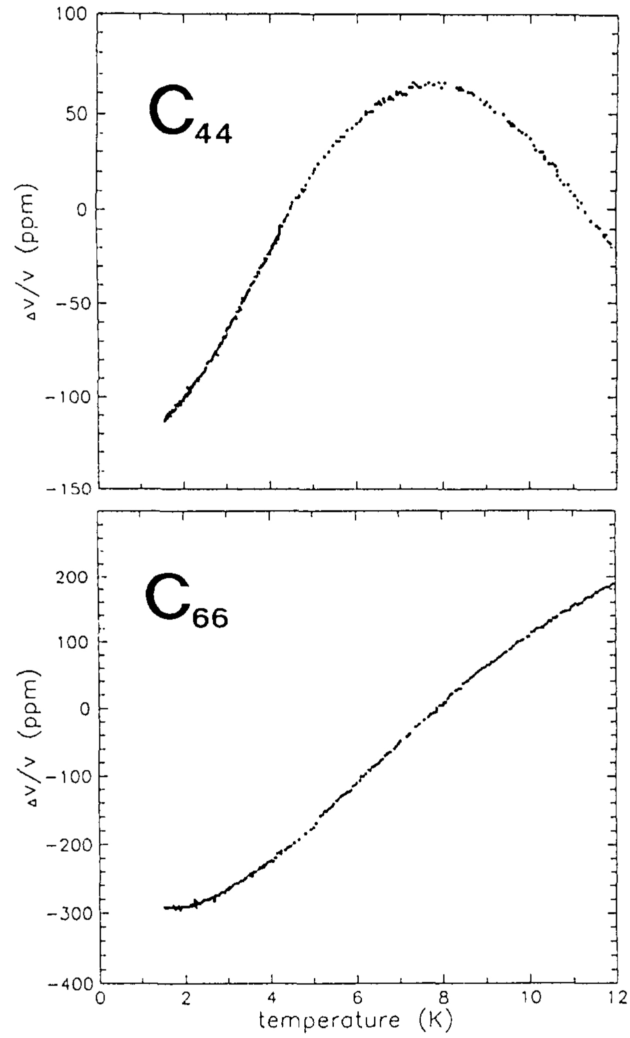

Fig. 4. Normalized temperature-dependent sound velocity of transverse sound of 20 MHz polarized parallel (C_{44}) and perpendicular (C_{66}) to the hexagonal axis.

This contradictionary situation has been one of the main reasons to investigate the cross-over from the high temperature state, which is assumed to be fully developed at ambient temperatures, and the HF state below about 10 K. Since ultrasonic studies of the elastic behaviour lead to information about the actual system state quite directly, extensive measurements of the temperature-dependent sound velocity for various crystal orientations and differently polarized sound waves were carefully performed. In particular, taking into account the macroscopic size (about 1 cm^3) of the single crystals investigated as well as the rather low temperature conductivity (proportional to thermal conductivity divided by specific heat) of this compound, which is even less than that of stainless steel, homogeneous cooling requires comparatively low cooling rates. The fact that the cooling conditions are indeed essential for the elastic behaviour actually observed soon became obvious when comparing the temperature-dependent sound velocity of the same elastic mode for different cooling rates.

4. Elastic behaviour below room temperature

In Fig. 5 the temperature dependence of the longitudinal modes C_{11} and C_{33}, which can be excited perpendicular and parallel to the hexagonal crystal axis respectively, is shown below 80 K. Both modes are obtained for rather low cooling rates as indicated and give evidence for significant changes in the system properties below about 20 K. The kink-like features occurring near 15 K mainly arise as consequence of a more or less sudden loss of lattice stability. Thus the anomalous temperature dependence shown reflects in part a non-equilibrium behaviour, *i.e.* time-dependent effects are also relevant and responsible for the transition

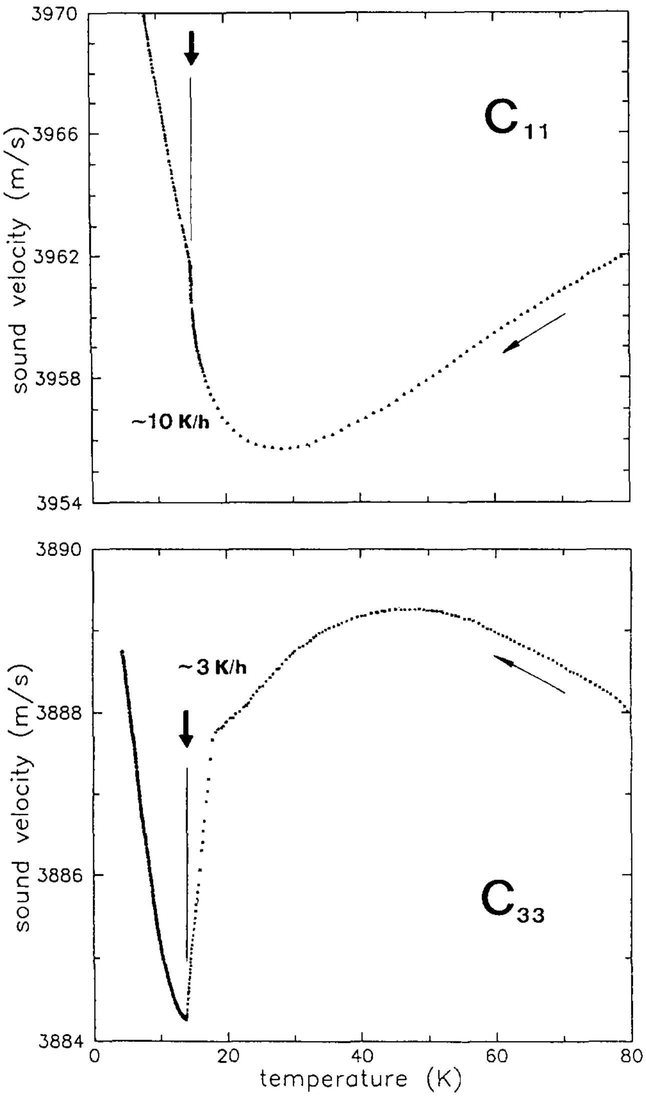

Fig. 5. Temperature-dependent sound velocity for longitudinal modes C_{11} and C_{33} (30 MHz) with slow cooling.

actually observed. The system behaves quite unstably in particular below 20 K. Upon cooling, it reacts more and more sensitively to external perturbations, so that finally the transition can be triggered even by "increasingly small" temperature fluctuations. Consequently a lower critical temperature exists which cannot be passed by the system conserving its high temperature state. Without having any detailed ideas at present about the physics involved, one can nevertheless clearly state that the strange behaviour observed is not reminiscent of continuous or second-order phase transitions.

As already mentioned, the actual course of the temperature-dependent sound velocity depends sensitively on the cooling conditions too. This gives rise to hysteretic effects in all elastic coefficients investigated over a broad temperature interval of at least 100 K. As a representative example the temperature dependence of the transverse mode C_{44} at various cooling rates is shown in Fig. 6. It should be emphasized that warming up from temperatures lower than 15 K, irrespective of the heating rate chosen, always results in a temperature dependence which fits well with those of the fastest cooling runs. Thus complete temperature cycles between room temperature and $T<15$ K contain pronounced hysteresis loops provided that slow cooling is carried out. On the high temperature side the thermoelastic hysteresis opens continuously between 200 K and 150 K. In contrast, the hysteresis is sharply closed at the latest near 15 K, sometimes accompanied by sudden erratic changes in the temperature-dependent sound velocity during cooling, reflecting the high lattice instability attained.

Both the thermoelastic hysteresis and the increasing sensitivity to perturbations upon slowly cooling the

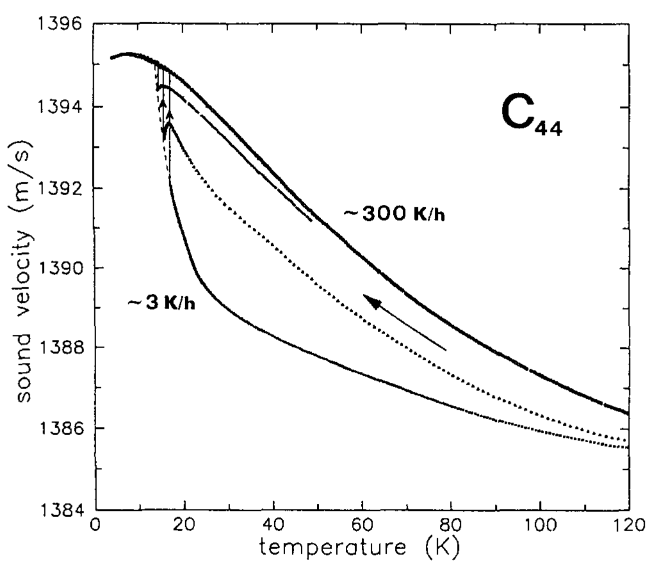

Fig. 6. Temperature dependence of transverse sound velocity for C_{44} mode (20 MHz) at various cooling rates between 3 and 300 K h^{-1}.

samples are strongly suggestive of undercooling phenomena and therefore indicative of a first-order phase transition below room temperature. Accordingly the lower bound at about 15 K should be regarded as a critical temperature of spinodal type which defines the absolute low temperature limit of stability of the parent phase. Furthermore, from Fig. 6 it becomes obvious that the actual state achieved by the system within the hysteretic region is very dependent on the thermal history, so that any state between the limiting cases can be met in principle for a given temperature. Consequently one would expect that these intermediate states originate in the coexistence of both a high temperature and a low temperature phase, which is also indicative of heterogeneous nucleation. In addition, the cooling conditions play such an important role as reflected by the thermoelastic behaviour that it seems reasonable to conclude that this phase transition is also heavily influenced by thermal stress, which can be easily obtained in this system by means of higher cooling rates.

The importance of thermal stress in the transition dynamics can be nicely demonstrated by applying short heat pulses to the sample from an electric heater. A little above the lower critical temperature (see Fig. 7) the heat pulses cause significant changes in the behaviour of the temperature-dependent sound velocity during slow cooling at about 3 K h^{-1}. Although the mean tendency is nearly conserved, small step-like features give notice of instantaneous and obviously irreversible changes due to short heating of the sample from the surface. This high sensitivity to external perturbations as well as the "athermal" and instantaneous response of the system is very reminiscent of structural transformations, especially those of martensitic type.

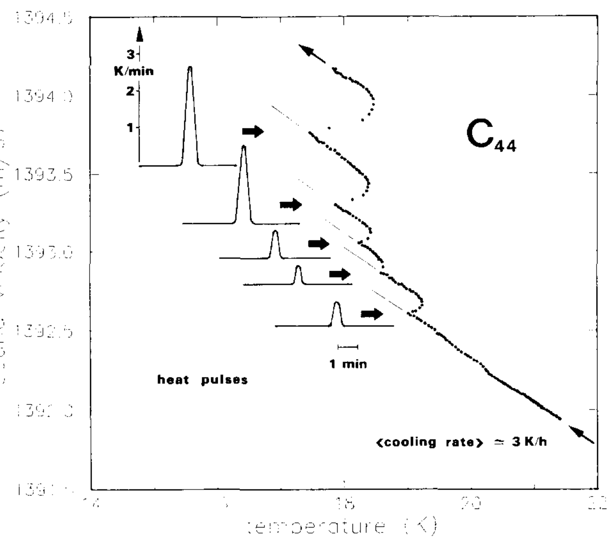

Fig. 7. Behaviour of temperature-dependent sound velocity (C_{44} mode at 20 MHz) slightly above the lower critical temperature at a mean cooling rate of about 3 K h^{-1}. Short heating of the sample at certain temperatures as sketched in the insets leads to nearly instantaneous and irreversible changes in the temperature course.

5. Conclusions

In order to get a deeper insight, investigations on a microscopic level are of course desirable, but some important comments can already be given. Comparing both the room temperature state and the state below 15 K, disregarding the uncertainties in the hysteretic region, no symmetry breaking could be detected elastically. On the scale considered the system behaves in both states as one of hexagonal symmetry. From thermal expansion measurements [27] it is known that the volume decreases only moderately (less than 10^{-5} K^{-1}) upon cooling from ambient temperature to 15 K. Hence the volume is only marginally influenced by the phase transition, which *e.g.* is in sharp contrast with the volume collapse of more than 10% accompanying the isostructural phase transition in Ce. The phase transition in UPt_3 is therefore most probably due to an isomorphic but nearly volume-conserving transformation of the lattice, which *e.g.* might be combined with regular changes in the stacking sequence of the hexagonal layers and would modify the local symmetry of the U ions essentially.

Although far from being well understood at present, the discovery of a first-order phase transition directly preceding the formation of the HF state in UPt_3 has shed some new light on the complex physics involved. In particular, the cross-over to a highly correlated ground state obviously takes place in a discontinuous manner and avoids the inherent instability due to volume contraction accompanying the Kondo mechanism often found in HF systems. Since the pronounced changes observed in the elastic coefficients above 15 K are more likely due to anisotropy than to volume effects, one might attribute them to electronic transitions between states of different configurational order. The latter should be closely connected with nearly volume-conserving changes in the composition of the intra-atomic f-excitations and the hybridizing band states. However, the formation of a heavy quasi-particle band requires beyond that phase-coherent charge excitations over the delocalization length of the conduction electrons. Since there exists experimental evidence that the f-electrons are both highly correlated [28] and yet itinerant [29] at low temperatures, UPt_3 seems to be at the border of intermediate valence compounds and therefore valence changes of the uranium (5f) ions cannot be excluded *a priori*.

References

1 G.R. Stewart, *Rev. Mod. Phys., 56* (1984) 755.
2 P.A. Lee, T.M. Rice, J.W. Serene, L.J. Sham and J.W. Wilkins, *Comments Condens. Matter Phys. XII, 99* (1986) 99.
3 P. Fulde, J. Keller and G. Zwicknagel, *Solid State Phys., 41* (1988) 1.
4 M. Sigrist and K. Ueda, *Rev. Mod. Phys., 63* (1991) 239.
5 V. Müller, C. Roth, D. Maurer, E.W. Scheidt, K. Lüders, E. Bucher and H.E. Bömmel, *Phys. Rev. Lett., 58* (1987) 248.
6 B.S. Shivaram, Y.H. Jeong, T.F. Rosenbaum and D.G. Hinks, *Phys. Rev. Lett., 56* (1986) 1078.
7 G. Bruls, D. Weber, B. Wolf, P. Thalmeier, B. Lüthi, A. deVisser and A.A. Menovsky, *Phys. Rev. Lett., 65* (1990) 2294.
8 S. Adenwalla, S.W. Lin, Q.Z. Ran, Z. Zhao, J.B. Ketterson, J.A. Sauls, L. Taillefer, D. Hinks, M. Levy and B.K. Sarma, *Phys. Rev. Lett., 65* (1990) 2298.
9 N. Grewe and F. Steglich, in K.A. Gschneidner Jr. and L. Eyring (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 14, North-Holland, Amsterdam, 1991, p. 343.
10 N. Lingg, *Diploma Work*, Freie Universität Berlin, 1993.
11 D.K. Wohlleben and B.R. Coles, in G.T. Rado and H. Suhl (eds.), *Magnetism*, Vol. 5, Academic, New York, 1973, p. 3.
12 G. Grüner and A. Zawadowski, in D.F. Brewer (ed.), *Progress in Low Temperature Physics*, Vol. VIIB, North-Holland, Amsterdam, 1978, p. 591.
13 J.W. Allen and R.W. Martin, *Phys. Rev. Lett., 49* (1982) 1106.
14 P. Thalmeier and B. Lüthi, in K.A. Gschneidner Jr and L. Eyring (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 14, North-Holland, Amsterdam, 1991, p. 225.
15 J.M. Luttinger, *Phys. Rev., 119* (1960) 1153.
16 H.R. Ott, in D.F. Brewer (ed.), *Progress in Low Temperature Physics*, Vol. XI, North-Holland, Amsterdam, 1987, p. 215.
17 Z.Fisk, D.W. Hess, C.J. Pethick, D. Pines, J.L. Smith, J.D. Thompson and J.O. Willis, *Science, 239* (1988) 33.
18 V. Müller, D. Maurer, K. deGroot, E. Bucher and H.E. Bömmel, *Phys. Rev. Lett., 56* (1986) 248.
19 S.W. Lin, S. Adenwalla, J.B. Ketterson, M. Levy and B.K. Sarma, *J. Low Temp. Phys., 89* (1992) 217.
20 B. Lüthi, *J. Magn. Magn. Mater., 52* (1985) 70.
21 V. Müller, D. Maurer and K. deGroot, *Physica B, 148* (1987) 73.
22 M.H. Cohen, M.J. Harrison and W.A. Harrison, *Phys. Rev., 117* (1960) 937.
23 A.B. Pippard, *Proc. R. Soc. A, 257* (1960) 165.
24 A.C. Hewson, *The Kondo Problem to Heavy Fermions*, Cambridge University Press, Cambridge, 1993.
25 M. Niksch, B. Lüthi and K. Andres, *Phys. Rev. B, 22* (1980) 5774.
26 D. Weber, M. Yoshizawa, I. Kouroudis, B. Lüthi and E. Walker, *Europhys. Lett., 3* (1987) 827.
27 A. deVisser, J.J.M. Franse and A. Menovsky, *J. Phys. F: Met. Phys., 15* (1985) L53.
28 R. Osborn, K.A. McEwen, E.A. Goremychkin and A.D. Taylor, *Physica B, 163* (1990) 37.
29 L. Taillefer and G.G. Lonzarich, *Phys. Rev. Lett., 60* (1988) 1570.