

Crystal-field effects in the magnetic and thermal properties of URu₂Si₂

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Specific-heat and thermal-expansion data for URu₂Si₂ are confronted with crystal-field calculations, using parameters based on a previous analysis of susceptibility data.

The discovery of antiferromagnetic order below 17.5 K and of superconductivity below 1 K (Refs. 1–3) in URu₂Si₂ has arisen great experimental interest in this compound. The magnetic, thermal, and transport properties have been studied by a variety of techniques on single-crystalline samples.^{4,5} Large anisotropies have been observed in the susceptibility, the thermal expansion, and the electrical resistivity. As regards the results of neutron diffraction studies^{6–8} of related compounds of the 1-2-2 series, it is clear that magnetic ordering along the *c* axis is a general feature in this series of compounds. The magnetic ordering in this series agrees rather well with a model of singlet-singlet-induced ordering as described, for example, by Wang and Cooper.⁹

Recently, a crystal-field calculation has been performed by Nieuwenhuys¹⁰ for URu₂Si₂ as well as UPt₂Si₂ in order to account for the temperature dependence of the susceptibility and the field dependence of the magnetization at 4.2 K for field directions parallel and perpendicular to the tetragonal axis. The susceptibility data of UPt₂Si₂ point to a level scheme with a singlet ground state and excited states at 39 K (singlet) and 56 K (doublet). Another excited state at 84 K does not couple magnetically to the other states and does not contribute to the susceptibility and the magnetization, although it is relevant for the specific heat. This level scheme provides a very satisfying fit of the susceptibility data parallel and perpendicular to the tetragonal axis and will be checked in magnetization measurements at 4.2 K in magnetic fields up to 40 T. This type of magnetization measurement has already been performed on URu₂Si₂ and served as a check on the crystal-field fit to the data for the temperature dependence of the susceptibility along the different crystallographic axes. In contrast to UPt₂Si₂, the susceptibility versus temperature curve of URu₂Si₂ along the tetragonal axis exhibits a rather broad peak around 50 K. The calculated curve, with, in this case, excited levels at 42 K (singlet), 169 K (singlet, nonmagnetic), and 550 K (doublet), reveals a much sharper maximum around 50 K. A calculation of the magnetization curves of URu₂Si₂ at 4.2 K in magnetic fields up to 40 T presents some quantitative agreement with the experimentally observed curves. The experimental data, however, show a sudden increase in the magnetization in a two-step process between 36 and 40 T,⁴ whereas the differential susceptibility, according to the calculations, reaches maximal values between 30 and 35 T.

Although the susceptibility and magnetization data and

even the value of 17.5 K for the antiferromagnetic ordering temperature are, at least in a qualitative way, compatible with a crystal-field calculation, the calculated value for the magnetic moment per uranium atom of $2.9\mu_B$ near zero temperature largely exceeds the value for the magnetic moment derived from neutron diffraction experiments¹¹ ($\mu \cong 0.03\mu_B/\text{U atom}$). Understanding this strong reduction in the magnetic moment goes beyond the possibilities of the crystal-field calculations.

In this contribution we continue with a crystal-field type of description by calculating the contribution of the proposed level scheme of URu₂Si₂ to the specific heat and by comparing experimental data for the specific heat and the thermal expansion with the calculated specific-heat results.

As far as the experimental specific-heat data are concerned, we make use of the results presented by Schlabitz *et al.*² for the difference in specific heat ΔC between URu₂Si₂ and ThRu₂Si₂ (see Fig. 1). Apart from a peak in ΔC at 17 K, a broad anomaly is found around 30 K with a ΔC value at 30 K of $\sim 4.6 \text{ J/mol K}$, approximately. The crystal-field calculations, not taking into account the magnetic interactions, reveal a comparable structure with reduced values for the maximum value of ΔC (3.3 J/mol K) around 18 K (see also Fig. 1). Upon increasing temperatures the calculated values for ΔC show a weak temperature dependence, reaching a value of 3.7 J/mol K at 100 K. The experimental value for the total specific heat at 100 K is about 100 J/mol K ,¹² show-

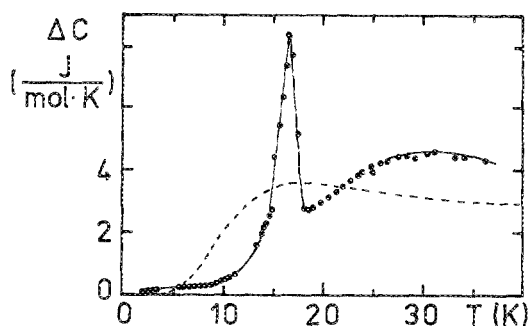


FIG. 1. Difference in specific heat between URu₂Si₂ and ThRu₂Si₂, ΔC , as a function of temperature [experimental data from Schlabitz *et al.* (Ref. 2)]; the broken curve represents a crystal-field contribution according to a level scheme with a ground-state singlet and excited states at 42 K (singlet), 169 K (singlet), and 550 K (doublet) (see Ref. 10).

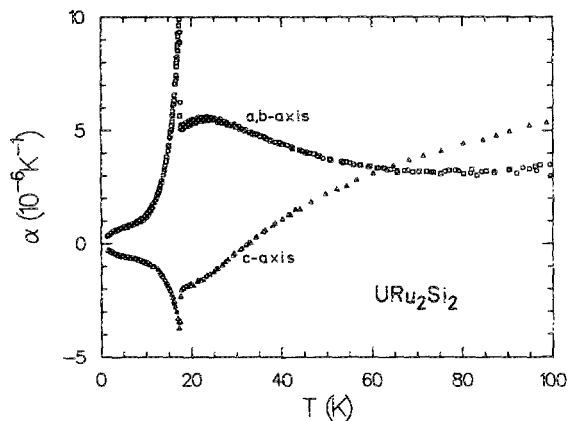


FIG. 2. Thermal expansion coefficient α ($=L^{-1}\Delta L/\Delta T$) along the three crystallographic axes of the tetragonal compound URu_2Si_2 : a axis (\circ); b axis (\square); c axis (\triangle); data taken from De Visser *et al.* (Ref. 12).

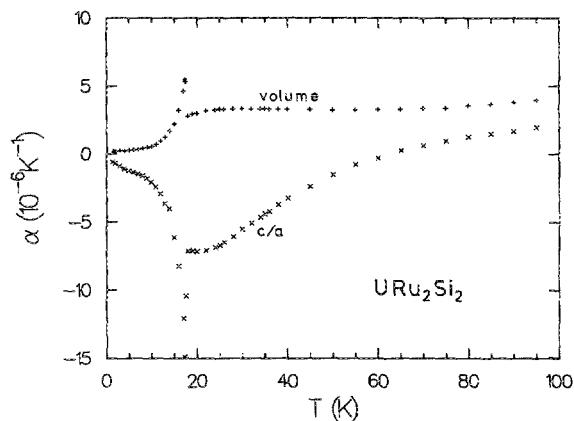


FIG. 3. Volume thermal expansion coefficient $\alpha_v = (\alpha_a + \alpha_b + \alpha_c)/3$ ($+$) and the relative temperature dependence of the c/a ratio $\alpha_r = (\alpha_c - \alpha_a)$ (\times), as determined from the data of Fig. 2.

ing that the crystal-field contribution is only a small fraction of the total specific heat at this temperature. An accurate experimental determination of ΔC over a large temperature interval is very difficult for that reason.

Another approach to separate the different contributions to the specific heat is sometimes provided by comparing specific-heat and thermal-expansion data. See, for instance, the analysis of the crystal-field contributions to specific heat and thermal expansion in $ErCu_2$.¹³ In particular, in cases where the different contributions to specific heat and thermal expansion are related by largely different values for the appropriate Grüneisen parameters, such an approach can be of help.

Thermal expansion data are shown in Fig. 2 for the different crystallographic directions of URu_2Si_2 in the temperature range between 1.5 and 100 K. From these results the volume expansion coefficient α_v [defined as $(\alpha_a + \alpha_b + \alpha_c)/3$] has been determined (see Fig. 3). In the temperature dependencies of α_a , α_b , and α_v maxima can be discerned between 20 and 40 K. In fact, up to temperatures of 40 K the experimentally observed values for α_v show the same type of temperature dependence as the above discussed calculated ΔC values, suggesting that the crystal-field contributions to the thermal expansion are dominating in this temperature interval. On the basis of a value of two for the electronic and lattice Grüneisen parameters, we indeed calculate electron and phonon contributions to the volume thermal expansion coefficient α_v of about $0.3 \times 10^{-6} \text{ K}^{-1}$ at 20 K, a value that is an order of magnitude smaller than the experimentally observed value for this parameter at 20 K [about $3 \times 10^{-6} \text{ K}^{-1}$ (see Fig. 3)], supporting the suggestion that crystal-field contributions to the thermal expansion are dominant at this temperature. In this calculation we assumed the electronic contribution to the specific heat to be given by γT , with a value for γ of 64 mJ/mol K, as determined at low temperatures. Taking a value of 25 for the electronic Grüneisen parameter as derived from a combination of specific-heat and thermal-expansion data below 2 K,¹² we still deduce a dominant crystal-field contribution to the volume thermal-expansion coefficient at 20 K. Upon further increasing the temperature up to 100 K, the value for

α_v is found to be weakly temperature dependent, reaching a value of $4 \times 10^{-6} \text{ K}^{-1}$ at 100 K. At this temperature, however, the phonon contribution to the volume expansion coefficient is expected to be at least of the same order of magnitude or even larger than the observed α_v value. We have to conclude for that reason that the crystal-field contributions to the thermal expansion arising from the higher excited levels must be of different magnitude or even of different sign. As regards the different symmetries of the crystal-field states, such a conclusion is not unreasonable. A quantitative interpretation of the thermal expansion data is, at present, out of our possibilities. The overall shape of the α_v versus the temperature curve, however, is considered to support a crystal-field type of approach for this material.

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