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High temperature susceptibilities of actinide monopnictides and monochalcogenides

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Abstract

The inverse susceptibilities of the monopnictides and monochalcogenides of the light rare earths plotted vs. temperature flatten off at high temperatures. This behaviour is well explained by Van Vleck paramagnetism of the excited states of the multiplet. For almost all actinide pnictides and chalcogenides a similar flattening-off is observed. Since spin orbit coupling is much stronger than in the light rare earth compounds an analogous interpretation is not possible. Susceptibility curves for uranium compounds can be fitted by adding a temperature dependent enhanced Pauli paramagnetism to the Curie–Weiss term (modified Curie–Weiss law). The high temperature susceptibility behaviour of neptunium compounds is very similar to uranium compounds i.e. an appreciable deviation from the Curie–Weiss law is only visible for the chalcogenides. The plutonium chalcogenides show a temperature independent paramagnetism, which can be explained either by a model of mixed valency, or by enhanced Pauli paramagnetism of non bond f-electrons. Americium compounds show up to room temperature a yet unexplained large temperature-independent susceptibility.

Keywords: Actinide monopnictides; Actinide monochalcogenides; Magnetism; Susceptibility

1. Introduction

The majority of the rare-earths and actinide monopnictides and monochalcogenides crystallize in the cubic NaCl structure. Since this structure is very simple and the interatomic distances are well above the Hill limit they arc ideal model substances for the study of the ionic properties [1].

The inverse magnetic susceptibilities of most of the above mentioned compounds follow the Curie–Weiss law up to room temperature. At higher temperatures a fattening out of the Curie Weiss line is observed for compounds of light rare and actinides. The analysis of such deviations are the topic of our work.

The susceptibilities of the Ce, Pr and Nd monochalcogenides and monopnictides, and their deviations from the Curie–Weiss law, are very convincingly explained by Van Vleck's theory. The energy differences between the ground- and the excited states of the multiplet are of the order of 2000 K, thus comparable to experimental temperatures [2]. The spin–orbit interactions in the heavy rare earth compounds are much stronger and no Van Vleck type of paramagnetism could by found at experimental temperatures.

Earlier, attempts were made to understand the magnetic susceptibilities and the ordered moments of actinides compounds on the basis of crystalline field effects. The postulated field splittings were calculated to be of the order of 1000 K for uranium [3] and americium [4] compounds. Such high values could never be found by any experiment and we know today that the crystal field splitting in uranium compounds e.g. is of the order of 100 K only [5].

The susceptibilities of all actinide pnictides and chalcogenides (the Pu chalcogenides excepted) can be fitted by the modified Curie–Weiss law:

$$\chi_{\text{measured}} = \frac{C}{T - \theta_{\text{para}}} + \chi_0 = \chi_{\text{Curie-Weiss}} + \chi_0 \qquad (1)$$

C is the Curie constant, θ_{para} the paramagnetic Curie temperature and χ_0 a generally temperature independent additional term. There are various possibilities for the explanation of this temperature independent additional paramagnetic term. Any imperfection of the sample will lead to a deviation from the Curie–Weiss law. As a rule we find that with increasing sample quality the reported χ_0 values are getting smaller. They are at a minimum for well defined single crystals. Values reported in the literature differ so by a factor of three or even more. In our table we therefore listed the lowest values, which are, as a rule the most recent results as well.

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An obvious reason for an observed intrinsic susceptibility is enhanced Pauli paramagnetism of quasi-free unbound electrons. The enhancement factor must be quite large i.e. the effective masses of such electrons is of an order of 20 as it has been shown for the case of US [5].

In the past few years a completely new concept for the understanding of the susceptibilities of actinide compounds was published, namely the that the actinide ion is in a mixed valence state. This idea was first applied to the interpretation of the temperature-independent paramagnetism of the plutonium chalcogenides [6]. Recently B.R. Cooper brought up the concept of 'leaking f-electrons' which means that we are dealing with two different kind of f-electrons [7].

2. Experimental methods

Our samples were single crystals grown in Zürich (rare earth and uranium) or in Karlsruhe (transurium). Measurements were done on one single crystal. In a few cases only two or three crystals had to be assembled in order to obtain the desired weight of the sample, which was typically 100 to 200 mg.

Measurements at low temperature were performed by the moving sample method. Inactive samples were enclosed in plexiglas containers, active sample had to be furthermore encapsulated in a german silver sealed tube. By this procedure we could make the measurements safely in a normal laboratory.

For the high temperature measurements we used the Faraday method. All samples were sealed into a thin wall quartz tube. The susceptibility of this container was found to be about 20% of sample susceptibility. Samples of the transurium compounds had to be further enclosed in sealed gold tubes. Unfortunately the signal of this double encapsulation became to be of the same order of magnitude as the sample signal. The measurements on active samples had to be done in a type A controlled laboratory at the Paul Scherrer Institut (PSI) in Villigen. The large contribution of the encapsulation and the uncertainty of the corrections which had to be done owing to it was a severe handicap. We performed all measurements with increasing and subsequently decreasing temperature. Good reliable measurements showed no thermal hysteresis.

3. Results

3.1. Lanthanide compounds

The susceptibilities of the monochalcogenides and monopnictides of the lanthanides follow the Curie–Weiss law. Deviations from it (at high temperatures) are encountered only for the compounds of Ce, Pr and Nd.

The rare-earth ions are in the trivalent state and the experimentally found magnetic moments can be calculated by assuming Russel–Saunders coupling. The susceptibilities of Ce, Pr and Nd have been measured and interpreted by the Van Vleck theory [2]. We have repeated and completed these earlier on measurements on well defined single crystalline samples. If the molecular field approach is considered to be valid we can eliminate the effect of the exchange interactions. The exchange field follows the rule $H_{ex} = \lambda M$. It can easily be seen that the exchange forces shift the inverse susceptibility curves by the factor λ. Fig. 1 shows that by an appropriate shift of the inverse susceptibilities we get an universal curve for all the pnictides and chalcogenides of neodymium. A. Furrer and P. Allensbach [8] have calculated this curve. The calculations are on Van Vleck interactions within the multiplet. The values for the intermultiplet splitting (first two excited states) were taken from spectroscopic data of the trichlorides. The important result is, that for both, the chalcogenides and the pnictides, the intermultiplet transitions are the same. Since Nd is undoubtedly in the trivalent state one free unbound electron is present in the chalcogenides. No influence of such unbound excess electrons is visible.

3.2. Uranium compounds

There is a distinct difference between the high temperature susceptibilities of the chalcogenides and the pnictides. This fact already rules out an interpretation which would be based on the above mentioned intermultiplet Van Vleck paramagnetism. Furthermore no excited multiplet states or crystal field transitions have been found experimentally up

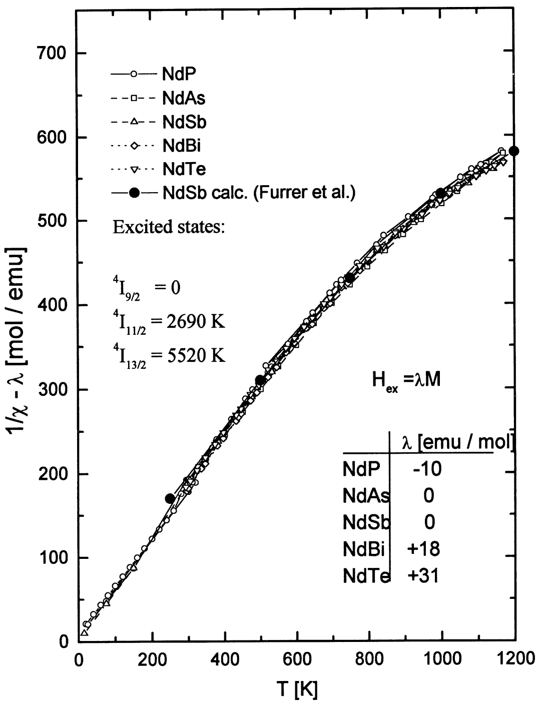

Fig. 1. Susceptibilities of Nd compounds normalized to zero exchange. Molecular field $H_{ex} = \lambda M$.

to energies of about 6 000 K [9], which means that spin–orbit coupling in actinide compounds is much stronger than in the corresponding light rare earths samples.

The high temperature magnetic susceptibility of US is understood by taking into account enhanced Pauli paramagnetism of unbound electrons. The susceptibility follows the law

$$\chi = \frac{C}{T - \theta_{\mathrm{para}}} + \chi_{\mathrm{Pauli}} \tag{2}$$

where the Pauli term is slightly temperature dependent:

$$\chi_{\mathrm{Pauli}} = \chi_0 \left(1 - \frac{\pi^2}{12}\left(\frac{T}{T_{\mathrm{F}}}\right)^2\right) = \chi_0(1 - cT^2) \tag{3}$$

The temperature dependence of χ_0 is due to the high effective masses of the electrons when the Fermi temperature T_{F} becomes comparable to the experimental temperature.

Fig. 2 shows the inverse susceptibility of UTe as a typical example of a chalcogenide. We see that an additional temperature-independent χ_0 (with a correction factor c) describes the experimental curve very well. It seems rather ambiguous to fit an experimental curve with 4 quasi-free parameters (θ_{para}, effective moment, χ_0 and c). Actually the choice for the values of these parameters is restricted since θ_{para} is defined by the low temperature Curie–Weiss law and c becomes effective only at very high temperature.

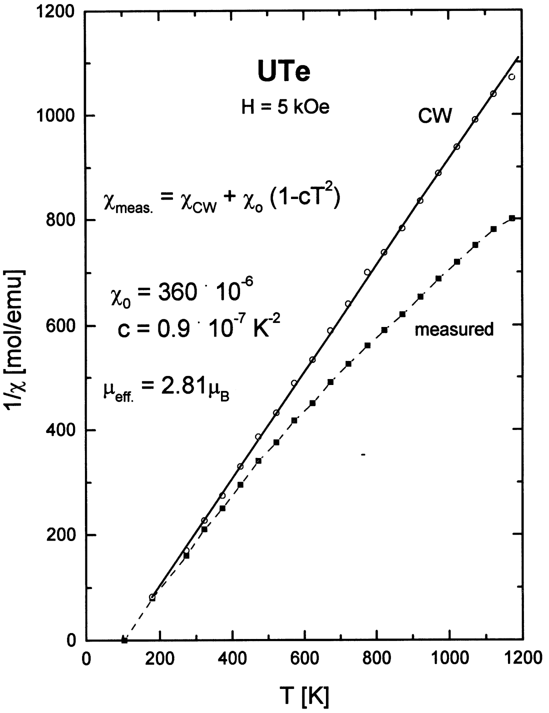

Fig. 2. Interpretation of the magnetic susceptibility of UTe by Pauli paramagnetism.

The effective moment and χ_0 are convincingly determined graphically by plotting

$$\chi_{\mathrm{measured}}(T - \theta_{\mathrm{para}})\ versus\ (T - \theta_{\mathrm{para}})$$

The resulting curve should be a straight line, if the modified Curie–Weiss law (Eq. (1)) is a good approximation. Such a plot is given in by Vogt et al. [10] for USe.

The high temperature susceptibilities of the uranium monopnictides have been measured earlier [11] and were found to follow the Curie–Weiss law up to 1000 K. We have repeated these measurements and have verified that indeed values of χ_0 are very low. Fig. 3 shows our results for UAs obtained on a single crystal.

The results of all measurements which were performed on uranium samples are in Table 1. It is very obvious that χ_0 is quite small for the pnictides but becomes important for the chalcogenides. The measured effective numbers of magnetons are not in accordance with calculations based on a model of a free trivalent uranium ion. A more elaborate theory is still needed.

3.3. Neptunium compounds

The findings are very similar to the results obtained for the uranium compounds. χ_0 values are small for the pnictides. As an example we show the measurements on NpAs in Fig. 4. The deviation from the Curie–Weiss law is very small. The opposite is the case for the chalcogenides: Fig. 5 shows that the of flattening-off is very important in the case of NpS but well explained by the modified

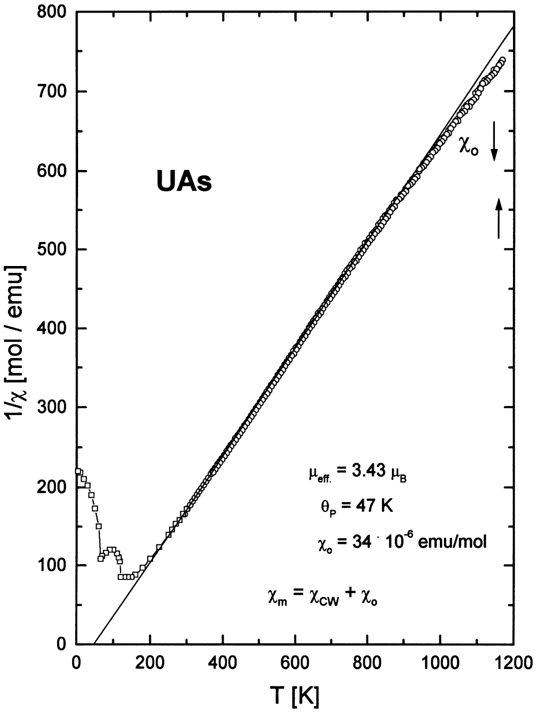

Fig. 3. Inverse molar susceptibility of UAs versus temperature.

Table 1
Measured values of χ_0 for actinide monopnictides and monochalcogenides, found for a modified Curie–Weiss law

	U	Np	Pu	Am	Y	La
N	109[a]	400[c]	250[b]	777[e]		
P	40	50	~50		10	
As	40	~25	~0	550[e]		
Sb	40	~20	30	1250[d]		
Bi		~20	60	500[e]		
S	370	160	260			40
Se	290		280			
Te	360		325	1500[e]	80	

$\chi_0(10^{-6}\ \text{emu mol}^{-1})$

$\chi_{\text{measured}} = \chi_{\text{Curie–Weiss}} + \chi_0$ (For Plutonium chalcogenides and the Americium compounds the Curie–Weiss term vanishes).

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Curie–Weiss law. The results of all neptunium compounds are in Table 1.

3.4. Plutonium compounds

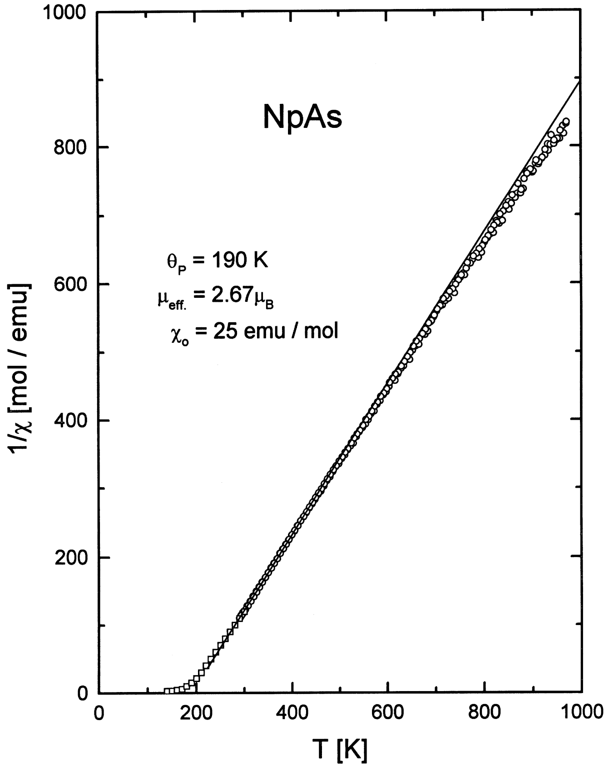

Fig. 4. Inverse molar susceptibility of NpAs versus temperature. (○, Faraday Balance; □, Moving Sample).

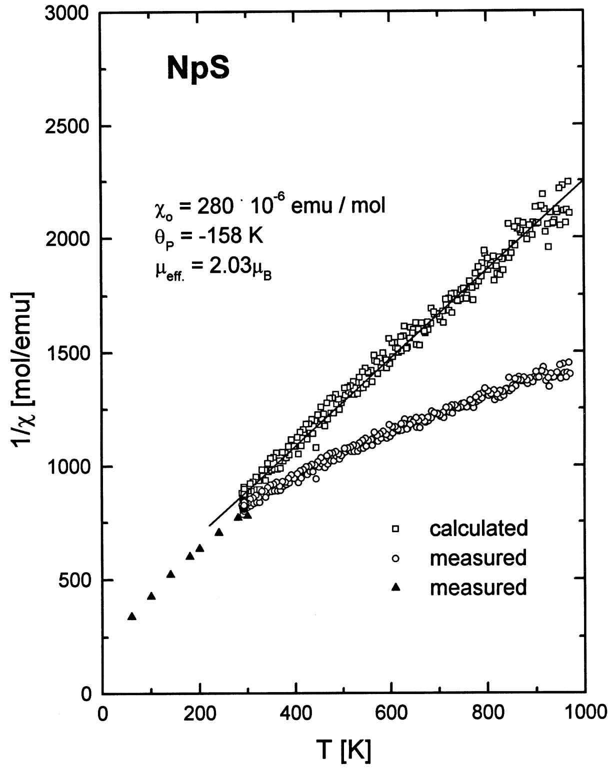

Fig. 5. Inverse molar susceptibility of NpS versus temperature. Triangles are data obtained from low temperature measurements on a small single crystal.

The effective magnetic moment of trivalent Pu is quite small. Thus the Curie–Weiss susceptibility of a free ion at 1000 K would be only about $125 \cdot 10^{-6}$ emu mol^{-1}. Even a minor contribution of a temperature-independent susceptibility is thus very easily seen. Fig. 6 shows our measurements on PuSb. The scattering of the points is unfortunately quite important due to the small signal of the sample and the large contribution of the encapsulation. Still we can see that χ_0 is quite small as it is for the rest of the pnictides (see Table 1).

The magnetic susceptibilities of the Pu chalcogenides were found to be almost temperature-independent between 50 and 300 K. [12]. This result was very convincingly explained by P. Wachter et al. [6] by a model of mixed valency. The valency of the plutonium ion is estimated to be about 2.75. Our new attempt to measure the susceptibilities at higher temperature has not yet yielded satisfactory results. Problems are the sensitivity of our equipment and the quality of the samples.

4. Discussion

In Table 1 we have summarized all actually available data. The χ_0 values reported in literature differ a great deal. It is not unreasonable to assume that the lowest reported values are the ones which describe best the intrinsic properties of a perfect sample.

Our measurements on the actinide compounds have

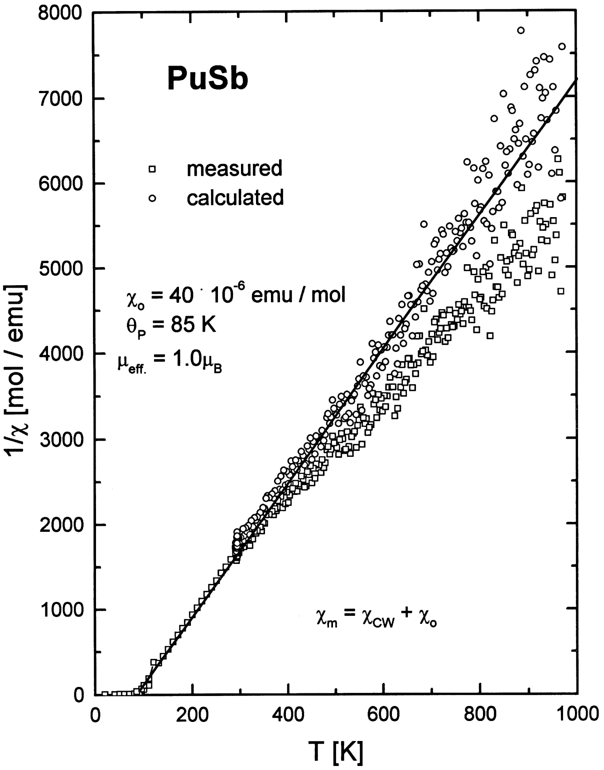

Fig. 6. Inverse molar susceptibility of PuSb versus temperature. The straight line shows a linear fit for calculated Curie–Weiss susceptibility.

made clear that the high temperature susceptibilities of the pnictides are basically different from the ones of the chalcogenides. The susceptibilities of the pnictides follow the Curie–Weiss law albeit the effective moments are not fully explained by a model of a free trivalent ion. Deviations from the Curie–Weiss law are relatively small and might easily be caused by the sample quality or by impurities. On the contrary the high temperature susceptibilities of the chalcogenides follow a Curie–Weiss law. The observed χ_0 value are certainly an intrinsic property which is due to the paramagnetism of quasi-free electrons. Explanations assuming mixed valency seem to be the most successful ones at present time.

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