Curie-Weiss behaviour of the paramagnetic susceptibility of $SmCu_2$

1992 J. Phys.: Condens. Matter 4 6859

(http://iopscience.iop.org/0953-8984/4/32/020)

J. Phys.: Condens. Matter 4 (1992) 6859–6861. Printed in the UK

COMMENT

Curie–Weiss behaviour of the paramagnetic susceptibility of $SmCu_2$

A M Stewart

Department of Applied Mathematics, Research School of Physical Sciences and Engineering, The Australian National University, GPO Box 4, Canberra 2601, Australia

Received 10 March 1992

Abstract. The Curie–Weiss temperature dependence of the paramagnetic susceptibility of polycrystalline $SmCu_2$ that has recently been measured by Gratz *et al* allows the exchange interaction between the 4f shell and the itinerant electrons to be estimated to be $+0.061 \pm 0.003$ eV.

It has been argued previously (Stewart 1972a, 1973) that there are theoretical grounds for supposing that the paramagnetic susceptibility χ of tripositive samarium materials can, in certain circumstances, obey a Curie–Weiss law:

$$\chi = \chi_0 + C/(T - \theta) \tag{1}$$

where the only dependence on temperature T is that shown explicitly. This expression is routinely used to characterize the paramagnetic properties of compounds with other tripositive rare earths, the information usually being given in the form of the effective paramagnetic moment p_{eff} where

$$C = N\mu_B^2 p_{\text{eff}}^2/3k \tag{2}$$

where N is the number of rare-earth atoms in the sample, μ_B is the Bohr magneton and k is Boltzmann's constant (Taylor 1971). The term in (1) that is independent of temperature is associated with the Landau and core diamagnetism and the Pauli susceptibility and, for materials that contain samarium, with Van Vleck paramagnetism.

It is not, on first consideration, apparent that the susceptibilities of other rare-earth materials should be expected to approximate to a Curie–Weiss law because of the presence of interaction effects beyond those taken account of by the mean-field approximation and because of crystal-field splittings. The former may be minimized by applying equation (1) to data at high temperatures where only mean-field effects remain. The latter are always present, except for S-state ions, and are typically of strength 100 K. However, it has been argued (Penny and Schlapp 1932, Stewart 1985) that while crystal fields may dominate the single-crystal susceptibility there is a sense in which their effects average out to a much smaller value in the polycrystalline susceptibility. It is the polycrystalline susceptibility from which the effective moment is obtained. If this can be taken to be the case, then any deviation of p_{eff} from the free-ion value p_0 of $g[J(J+1)]^{1/2}$ is due solely to the effects of itinerant-electron

0953-8984/92/326859+03$04.50

polarization. These are twofold: first there arises the electronic analogue of the nuclear Knight shift which acts to increase the magnetic polarization of the rare-earth ion; second the rare-earth ion induces a cloud of polarized itinerant electrons localized around it that adds to its moment (Stewart 1972a). For normal rare earths the change in effective moment is rather small, usually less than 10%, although there are exceptions such as the RCo_2 compounds, all of whose susceptibilities obey equation (1), in which the changes are much larger (Stewart 1983).

For materials that contain samarium the situation is even more complex because of the Van Vleck paramagnetism arising from the mixing of higher multiplet levels into the ground state by the applied fields. This mixing gives rise to a free-ion susceptibility of $b + a/T$ having the form of a temperature-independent term and a Curie term, where $b = N\mu_B^2 20/7\Delta$ and Δ is the splitting between the $J = \frac{7}{2}$ multiplet level and the $J = \frac{5}{2}$ ground state.

Despite this complication it was found (Stewart 1972a, 1973) that a calculation of the paramagnetic susceptibility of samarium materials below temperatures of about 250 K that takes account of interionic interactions, the effects of itinerant-electronic polarization but *not* crystal-field effects predicts the Curie–Weiss susceptibility of equation (1) with

$$p_{\text{eff}} = p_0[1 + \alpha(g-1)/g - (1+\alpha)\theta/T_0] \tag{3}$$

where $T_0 = -(g-1)a/gb$ is the White–Van Vleck (1961) crossover temperature ($T_0 = 322$ K) and $\chi_0 = \chi_M + b[1 - g\theta/(g-1)T_0](1+\alpha)^2$, χ_M being the matrix susceptibility. The quantity α, which reflects the effects of itinerant-electron polarization, is equal to $2I(0)\rho$ where $I(0)$ is the wavevector-dependent exchange interaction of form $-2I(q)S \cdot s$ between the rare-earth spin S and the itinerant electron spin s, q being the wavevector. The quantity ρ is the electronic density of states per atom for one spin direction.

The above expressions for p_{eff} and χ_0 are valid for normal rare earths as well, but for them T_0 is very large and $(g-1)/g$ is equal to or less than 0.5; so the change in effective moment is small. For samarium, however, $(g-1)/g = -2.5$ and the effect of itinerant polarization upon the effective moment is around five times that for normal rare earths; the term containing θ/T_0 is important too. For some samarium materials the effects are very large indeed; elemental samarium has a Curie constant that is almost a quarter of the free-ion value (Stewart 1981) and $SmCo_2$ a Curie constant that is more than eight times the free-ion value (Stewart 1983). SmZn even has a moment that is reversed in direction (Givord *et al* 1980), the possibility of which had been predicted earlier (Stewart 1972b). The paramagnetic susceptibility of a polycrystalline samarium material therefore provides a very sensitive probe of the strength of itinerant-electron effects in the material.

The only case yet in which a calculation of the susceptibility has been made which takes account of crystal-field effects, interactions and itinerant-electron polarization is of $SmRh_4B_4$ (Zhou *et al* 1987). Even though in this material itinerant-electron effects are unusually small (Stewart 1981), it was found that it was essential to include them to obtain a satisfactory description of the susceptibility (Zhou *et al* 1987).

Because of the complexities associated with the electronic structure of the samarium ion, some workers (de Wijn *et al* 1976) have concluded that in the case of Sm^{3+} a Curie–Weiss temperature dependence of the susceptibility would not be present under any circumstances. However, despite this pessimism, samarium compounds continue

to be reported whose polycrystalline susceptibilities are found *experimentally* to follow a Curie–Weiss law and whose effective moments provide consistent information about the effects of itinerant-electron polarization (Stewart 1983).

The points made above are illustrated by recent measurements that have been made on $SmCu_2$. Although the single-crystal susceptibility of this material is grossly anisotropic and has little Curie–Weiss-like dependence for any of the crystal directions (Isikawa *et al* 1988), the polycrystalline susceptibility is found to follow the form of equation (1) with $p_{\text{eff}} = 0.53$, $\theta = -14$ K and $\chi_0 = 1.07 \times 10^{-3}$ emu mol^{-1} (Gratz *et al* 1990). If these values are substituted into equation (3), the value of $+0.170$ is obtained for α.

A comparison may be made with $GdCu_2$ whose effective moment is 8.4 (Sherwood *et al* 1964). Again using equation (3), but with infinite T_0 because of the large multiplet separation, α for this material comes to $+0.11$. If it is arbitrarily assumed that the accuracy of measurement of the susceptibility is 5% (so the uncertainty in the effective moment is half this) the value of α for $GdCu_2$ is $+0.11 \pm 0.05$. If a similar accuracy is assumed for $SmCu_2$, then its α is $+0.170 \pm 0.007$. The two values are in agreement, but the value for $SmCu_2$ is of higher precision.

Finally, the term in the low-temperature specific heat of $SmCu_2$ that is linear in temperature has the value 20 mJ mol^{-1} K^{-1} (Gratz *et al* 1990); this leads to a density of states of $\rho = 1.4$ eV^{-1}/atom spin. From this the value of $+0.061 \pm 0.003$ eV is obtained for $I(\mathbf{0})$.

References

de Wijn H W, Van Diepen A M and Buschow K H J 1976 *Phys. Status Solidi* b **76** 11
Givord D, Morin P and Schmitt D 1980 *J. Magn. Magn. Mater.* **15–18** 525
Gratz E, Pillmayr N, Bauer E, Muller H, Barbara B and Lowenhaupt M 1990 *J. Phys.: Condens. Matter* **2** 1485
Isikawa Y, Mori K, Takeda H, Umehara I, Sato K, Onuki Y and Komatsubara T 1988 *J. Magn. Magn. Mater.* **76–7** 161
Penny W G and Schlapp R 1932 *Phys. Rev.* **41** 194; *Phys. Rev.* **42** 666
Sherwood R C, Williams H J and Wernick J H 1964 *J. Appl. Phys.* **35** 1049
Stewart A M 1972a *Phys. Rev.* B **6** 1985
—— 1972b *J. Phys. F: Met. Phys.* **2** L22
—— 1973 *Phys. Rev.* B **8** 2214
—— 1981 *Phys. Rev.* B **24** 4080
—— 1983 *J. Phys. C: Solid State Phys.* **17** 1557
—— 1985 *Phys. Rev.* B **32** 3331
Taylor K N R 1971 *Adv. Phys.* **20** 551
White J A and Van Vleck J H 1961 *Phys. Rev. Lett.* **6** 412
Zhou H, Lambert S E, Maple M B, Malik S K and Dunlap B D 1987 *Phys. Rev.* B **35** 594