MAGNETIC TRANSITION POINTS AND MAGNETIC MOMENTS IN SOME URANIUM COMPOUNDS

J. Ternberk, J. H_ebík, A. Me_ovský, Z. Smetana

MAGNETIC TRANSITION POINTS AND MAGNETIC MOMENTS IN SOME URANIUM COMPOUNDS

J. ŠTERNBERK, J. HŘEBÍK, A. MEŇOVSKÝ, Z. SMETANA
Faculty of Mathematics and Physics, Charles University, Prague, 2, Czechoslovakia

Résumé. — Les composés polycristallins U_3P_4, U_3As_4, U_3Sb_4, U_3Bi_4 et UGa_2 ont été étudiés par la méthode de la dépendance $\sigma^2 = f(H/\sigma)$ pour trouver les valeurs bien définies des températures de transitions magnétiques T_C et les valeurs des aimantations spontanées ($H_{max} \approx 50$ kOe, $T_{min} = 4{,}2$ °K). On a trouvé que les points T_C coïncidaient avec les points asymptotiques de transition sauf pour les composés U_3As_4 et U_3Sb_4. On a essayé d'expliquer la différence entre les moments atomiques obtenus en états magnétiques ordonnés et désordonnés.

Abstract. — Polycrystalline compounds U_3P_4, U_3As_4, U_3Sb_4, U_3Bi_4 and UGa_2 have been investigated by the method of the dependence $\sigma^2 = f(H/\sigma)$ to find well defined values of the magnetic transition temperatures T_C and the values of the spontaneous magnetizations ($H_{max} \approx 50$ kOe, $T_{min} = 4.2$ °K). It has been found that the points T_C coincide with the asymptotic transition points except the compounds U_3As_4 and U_3Sb_4. An attempt was made of explaining the difference between the atomic moments obtained in the ordered and disordered magnetic states.

As is known, direct methods for measuring the temperature dependence of magnetic moments may fail near the points of magnetic transition. Therefore, studying the magnetic properties of uranium compounds, the authors have tried to apply the method of σ^2 vs H/σ curves.

Polycrystalline samples of U_3P_4, U_3As_4, U_3Sb_4, U_3Bi_4 and UGa_2 in powder form have been prepared in vacuum by direct chemical reaction between stoichiometric amounts of their components [1]. Powdered U (nuclear), obtained by thermal dissociation of UH_3, and P, As, etc. of semiconductor purity were used. The samples were homogenized by very long annealing, set free from impurities by magnetic separation at liquid nitrogen temperature and checked by chemical analysis. Care was taken to protect the substances from the influence of the atmosphere.

As mixtures of U_3X_4 with UX or UX_2 (and UGa_2 with UGa or UGa_3) can appear the samples were quantitatively analyzed by X-ray diffraction. The following purities (in weight %) were found : 95 % for U_3As_4 and U_3Sb_4, 90 % for U_3P_4 and U_3Bi_4 and 80 % for UGa_2, but can be better for each compound. According to these data all magnetic quantities treated below have been corrected to represent the materials with 100 % purity.

The procedure of measurement and interpretation was based on the relation (see, e. g., Belov [2], Heyner and Kohlhaas [3] for thermodynamic derivation, and Lange et al. [4] for derivation from the molecular field model)

$$H_i/\sigma = a + b\sigma^2 + c\sigma^4 , \qquad (1)$$

where σ is the magnetic moment per unit mass (assumed small in the vicinity of the transition point), H_i the real field inside the material (high enough for complete domain alignment) and a, b, c are constants (at constant temperature and pressure). Due to low magnetic moments and high fields at the experiments the external field H could be used instead of H_i. The ballistic method of measurement has been described by the authors in [1].

Most thorough studies have been performed for U_3Sb_4. The experimental points of the isotherms σ^2 vs H/σ are shown in figure 1. As predicted by eq. (1), these isotherms can be approximated by parabolas although there is a variety of forms. By full parabolas an attempt is made of keeping the vertices on a line parallel to the H/σ-axis and the coefficient c from eq. (1) proportional to the absolute temperature T in complete agreement with the molecular field model [4], by dashed parabolas only the condition for the vertices is fulfilled. The coincidence of full and dashed parabolas at 149 °K was achieved by a suitable choice of the coefficients a, b, c in eq. (1). It can be concluded, however, that taking various possibilities of approximation has a negligible influence on finding the isotherm aiming at the origin and thus defining the transition temperature T_C (or Curie point, see [3], [4]).

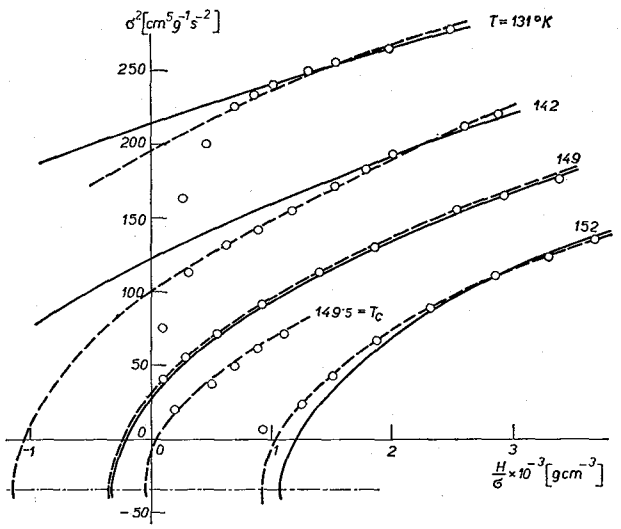

FIG. 1. — The isotherms σ^2 vs H/σ for U_3Sb_4. The points are experimental results, the full and the dashed curves are parabolical approximations (see main text). The dashed-and-dotted line shows the positions of the vertices. The isotherm at 149.5 °K has been measured in an electromagnet, the rest in a superconducting solenoid.

Even though a linear extrapolation from low-field measurements (i. e. up to $\approx$ 10 kOe) is used a deviation not more than 1 °K from the value of T_C can be expected supposing a fixed temperature scale (cf. isotherm at 149.5 °K in figure 1 and the results presented for classical ferromagnets by Belov [2]). Keeping this in mind we have deduced the temperatures T_C for the other compounds by the linear approximation (see Table I).

TABLE I

Compound	T_C (°K) $\pm$ 2°	Θ_C (°K) $\pm$ 2°	μ_σ(BM) $\pm$ 5 %	μ_χ(BM) $\pm$ 5 %
U_3P_4	144	145	—	2.70
U_3As_4	198	203	1.35	2.70
U_3Sb_4	149.5	154.5	1.55	3.05
U_3Bi_4	112	111	1.60	3.10
UGa_2	125.5	126	2.35	3.60

As an example figure 2 presents the temperature dependence of the spontaneous magnetization σ_s of U_3Sb_4 obtained both from the intersections of the isotherms σ^2 vs H/σ (Fig. 1) with the σ^2-axis [3], [4] and from high-field measurements of magnetic moments at different temperatures (see below). The advantage of the former method as to the approach of the $\sigma_s(T)$ dependence to the zero value (T_C point) is clearly seen. On the other hand, from the standpoint of general thermodynamic theory this method may be open to criticism (Fisher [5]).

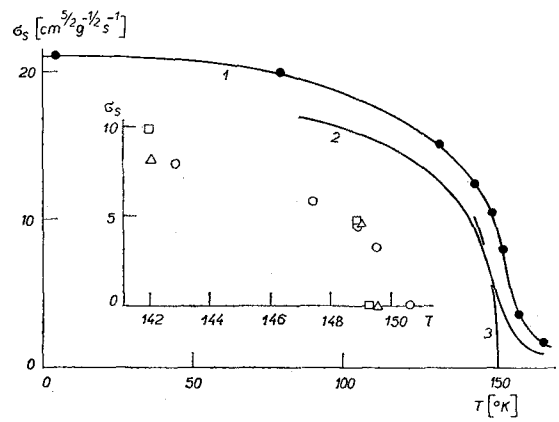

FIG. 2. — Temperature dependence of spontaneous magnetization σ_s for U_3Sb_4. Minor figure : results deduced from dependences in figure 1. □ — approximation in complete agreement with the molecular field model (full parabolas), △ — approximation with keeping the vertex condition only (dashed parabolas), o — linear approximation (not shown in figure 1). Main figure : 1, 2 — spontaneous magnetization from saturated moments (1 — our result, 2 — result of Trzebiatowski et al. [12]), 3 — dependence obtained by averaging the experimental values from the minor figure.

In addition to the values of T_C (see above) Table I contains also the asymptotic transition points Θ_C obtained by linear extrapolation from the dependences 1/susceptibility vs T in the region $T > T_C$. It is seen that either the points T_C and Θ_C coincide within the limits of experimental errors or there is a usual difference $\Theta_C - T_C > 0$. Thus, the differences $\Theta_C - T_C$, reported systematically + 2 °K for U_3Bi_4, U_3Sb_4 and U_3As_4 [6] or found even negative for $\beta - UH_3$ [7] and U_3P_4 [8], should be accepted with some caution.

Further, Table I presents magnetic moments per uranium atom (in Bohr's magnetons BM) both from the highfield (50 kOe) measurements at 4.2 °K (μ_σ) and from the temperature dependence of the susceptibility above the transition point (μ_χ). Evidently, the values of μ_σ by Trzebiatowski et al. at 85 °K [6], [9] are somewhat different, nevertheless, Trzebiatowski's conclusions, drawn from his values of μ_χ [9], keep their validity because of true dependence of these moments on the composition.

The relation $\mu_\chi \approx 2\,\mu_\sigma$ seems to be fulfilled for our moments of cubic compounds (U_3X_4). Using Buhrer's results [10], this can be explained as follows : In a magnetically ordered single crystal each third of magnetic atomic moments μ_χ (free for $T > T_C$) is rigidly coupled with one of the $< 100 >$ directions. Considering three atoms, this results in an effective magnetic moment $\mu_\chi \sqrt{3}$ in the $< 111 >$ direction, i. e. the effective magnetic moment per atom in the $< 111 >$ direction is $\mu_{eff} = \mu_\chi \sqrt{3}/3$. According to the experimental reality (extrapolation of magnetization isotherms to zero field intensities) the averaging procedure for a polycrystal means to multiply μ_{eff} by the factor $\sqrt{3}/2$ [11] so that for the observed μ_σ we have $\mu_\sigma = \mu_{eff} \sqrt{3}/2 = \mu_\chi/2$.

In conclusion, the authors wish to express their thanks to Dr V. Roskovec and F. Zounová (Inst. Solid State Phys., Czech. Acad. Sci.) for measurements in the superconducting solenoid, to V. Sechovský for data on paramagnetic susceptibilities and to E. Brunhoferová for assistance in preparing the manuscript.

References

[1] STERNBERK (J.), ANSORGE (V.), HŘEBÍK (J.), MEŇOVSKÝ (A.) and SMETANA (Z.), *Czech. J. Phys.* B, 1971, at press.

[2] BELOV (K. P.), Magnetic Transitions, Gos, izd. fiz. mat. lit., Moscow, 1959.

[3] HEYNER (K.) and KOHLHAAS (R.), *Zs. angew. Phys.*, 1969, **26**, 80.

[4] LANGE (H.), KOHLHAAS (R.) and ROCKER (W.), Magnetometrie and magnetokalorischer Effekt des Kobalts in der Umgebung der Curie-Temperatur, Westdeutscher Verlag, Köln u. Opladen, 1969.

[5] FISHER (M. E.), The Nature of Critical Points, University of Colorado Press, Boulder, Colorado, 1965.

[6] TRZEBIATOWSKI (W.), Ferro- und antiferromagnetische Eigenschaften von Uranverbindungen, in « Magnetismus », Deutscher Verlag für Grundstoffindustrie, Leipzig, 1967.

[7] LIN (S. T.) and KAUFMANN (A. R.), *Phys. Rev.*, 1956, **102**, 640.

[8] WARREN (I. H.) and PRICE (C. E.), *Canad. Metal. Quart.*, 1964, **3**, 245 (according to FRIEDMAN (F.), GRUNDZWEIG (J.) and KUZNIETZ (M.), *Physics Letters*, 1967, **25A**, 690).

[9] TRZEBIATOWSKI (W.) and ZYGMUNT (A.), *Bull. Acad. Polon. Sci.*, s. sci. chim., 1966, **14**, 495.

[10] BUHRER (C. F.), *J. Phys. Chem. Solids*, 1969, **30**, 1273.

[11] GANS (R.), *Ann. Physik*, 1932, **15**, 28.

[12] TRZEBIATOWSKI (W.), SEPICHOWSKA (A.) and ZYGMUNT (A.), *Bull. Acad. Polon. Sci.*, s. sci. chim., 1964, **12**, 687.