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LOW-TEMPERATURE PHASE TRANSITIONS AND MAGNETIC SUSCEPTIBILITIES OF LOW-DIMENSIONAL URANIUM FLUORIDES

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UDC 546.16:541.66

Measurements have been made on the magnetic susceptibilities of the quasi-one-dimensional magnetic α-UF_5 and the cluster magnetic U_2F_9 (a four-nuclear type) over the range 4.2-300 K. The Curie–Weiss law applies for α-UF_5 above 200 K, with $\mu_{ef} = 2.37\mu_B$, $\theta = -148$ K; that law also applies to U_2F_9 above 150 K, with $\mu_{ef} = 2.9\mu_B$ and $\theta = 118$ K. The antiferromagnetic ordering is discussed for the one-dimensional chains in α-UF_5 together with the phase transition observed in U_2F_9 at 6 K. It is assumed that the U^{4+} and U^{5+} valency states are stabilized below the phase-transition point, and only then can U_2F_9 be considered as the compound $UF_4 \cdot UF_5$.

Spin cluster compounds and quasi-one-dimensional and quasi-two-dimensional ones are familiar for the d elements. Out of compounds of the F elements, only the uranium fluorides α-UF_5 and U_2F_9 have structures corresponding to quasi-one-dimensional and cluster magnetics. The magnetic parameters of these have not been examined. In general, the magnetochemical parameters of uranium compounds have been inadequately examined. In particular, among the fluorides, we have data only for UF_4 [1] and β-UF_5 [2]. Here we present results on the magnetic susceptibilities of the major representatives of the higher paramagnetic uranium fluorides α-UF_5 and U_2F_9 over the range 4.2-300 K.

The α-UF_5 was made by direct fluorination of uranium tetrafluoride with elemental fluorine at 420 K, while U_2F_9 was made by reacting UF_4 with uranium hexafluoride at 520 K. The initial UF_4 was made by reducing uranium hexafluoride with silicon at 590 K. The fluorine was purified from oxygen by rectification [3]. The α-UF_5 and U_2F_9 were identified by x-ray analysis.

The measurements were made by Faraday's methods over the range 4.2-300 K. A specimen of mass 60 mg was sealed into a silica tube. The empty tube was measured separately subsequently. The value of χ for this was incorporated in calculating the susceptibility. The diamagnetic correction was derived from an additive scheme via the data of [4]. The measurements were made in fields of 0-10.9 kOe. There was a weak $\chi(H)$ dependence evidently caused by traces of ferromagnetic materials, in particular iron or nickel. Figure 1 shows the observed temperature dependence of the susceptibility for α-UF_5; χ behaves nonlinearly below 200 K, while above it the Curie–Weiss law applies:

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0022-4766/86/2706-0898$12.50

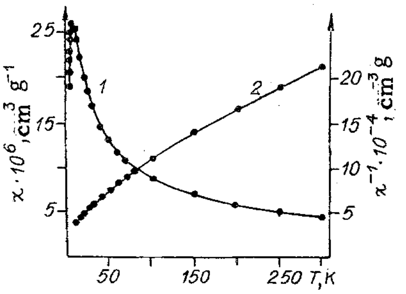

Fig. 1

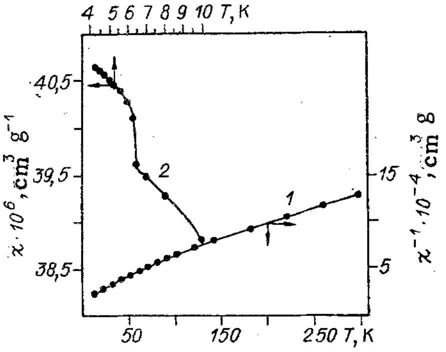

Fig. 2

Fig. 1. Dependence of the specific susceptibility χ (curve 1) and χ^{-1} (curve 2) on temperature for α-UF_5.

Fig. 2. Temperature dependence of the specific magnetic susceptibility for U_2F_9: 1) $\chi^{-1}(T) = 10$-300 K; 2) $\chi(T) = 4.2$-10 K.

$$\chi = \frac{C}{T-\theta}$$

with parameters $\mu_{ef} = \sqrt{8C} = 2.37\mu_B$ and $\theta = -148$ K.

The susceptibility does not follow the Curie–Weiss law at low temperatures, and there is a peak in χ at 6.3 K, which may be related to antiferromagnetic ordering in the one-dimensional chains. The contribution from the orbital moment is not small for U^{5+} (terms $^2F_{5/2}$ and $^2F_{7/2}$), which can lead to substantial anisotropy in the exchange interaction. The exact solution for a one-dimensional Ising chain is [5]

$$\chi = \frac{N\bar{\mu}^2}{kT} e^{2J/kT},$$

$$\bar{\mu} = g\beta,$$

where g is the factor and β is the Bohr magneton.

The observed χ are compared with the theoretical values for 4.2-20 K to derive the optimum parameters $J = -2.84$ cm^{-1} and $g = 0.718$. This g factor differs from the pure spin value, which indicates that a pure Ising chain model is not applicable for α-UF_5. Susceptibility calculations for the linear Heisenberg chain led Bonner and Fisher [6] to estimate the exchange interaction parameter ($S = 1/2$) for U^{5+} ions. The theory gives the following relations for an antiferromagnetic chain:

$$|J|\chi_{\max}/Ng^2\beta^2 = 0.07346; \quad kT(\chi_{\max})/|J| = 1.282.$$

On using the observed $\chi = 8685 \cdot 10^{-6}$ cm^3·mole^{-1} and $T(\chi_{\max}) = 6.3$ K, we get $|J| = 4.189$ cm^{-1} and $g = 1.376$.

Therefore, neither the Heisenberg one-dimensional chains nor the Ising ones give a satisfactory description of the observed behavior of the susceptibility of α-UF_5, which may indicate a substantial contribution from chain interaction. The theoretical $\chi(T)$ curve [6] for the range 4.2-20 K describes the observed result satisfactorily; the observed and theoretical values of χ deviate substantially at $T > 20$ K. The nonlinear behavior of $\chi^{-1}(T)$ below 100 K is due evidently to the joint action of the octahedral field and the spin-orbit interaction, which displaces the $^2F_{5/2}$ and $^2F_{7/2}$ multiplets, and this is also responsible for θ being larger than the temperature of antiferromagnetic ordering. Only combined incorporation of the exchange interactions and the splittings for U^{5+} can explain the results. The effects from excited states lead to an additional temperature-independent (van Vleck) contribution to the susceptibility. We have incorporated the nonlinearity of $\chi^{-1}(T)$ by introducing this term via the formula

$$\chi = \frac{C}{T-\theta} + \chi_{VV}.$$

The best agreement with experiment is attained with $C = 0.454$, $\chi_{VV} = 321 \cdot 10^{-6}$ cm^3·mole^{-1}, $\mu_{ef} = 1.914$, and $\theta = -70$ K.

Figure 2 gives the observed susceptibility of U_2F_9; the structure contains four-nuclear U_4F_{18} clusters, in which the two U^{4+} atoms and the two U^{5+} ones are localized at the structurally equivalent vertices of a regular tetrahedron. Strictly speaking, this compound has fractional valency at ordinary temperatures, while the black color is due to the rapid $f^1 \rightleftarrows f^2$ electron migration. The six bridge fluorine atoms lie near the edges of the tetrahedron, while the other 12 fluorine atoms supplement the coordination polyhedra for each of the uranium atoms to octahedra. There is close packing of the U_4F_{18} particles. In such a four-nucleus cluster consisting of ions of variable valency, U^{4+} and U^{5+}, which have configurations f^1 and f^2, one expects to find spin ordering and unpaired-electron localization at low temperatures [6, 7, 9]. No signs of magnetic ordering have been observed throughout the temperature range used (curve 1 in Fig. 2), which may mean either that the exchange constant is very small or that spin localization effects are too strong [8]. There is a step change in the susceptibility at 6 K (curve 2 in Fig. 2). One assumes that the change is due to a structural phase transition on account of localization and ordering for the f^1 and f^2 electrons. The localization reduces the initial high symmetry of the crystal and stabilizes the U^{4+} and U^{5+} in two structurally nonequivalent positions.

The general argument can be given on the trend in $\chi(T)$ in this transition (neglecting the effects of structure change in the environment of the uranium ion). The unpaired-electron localization on the U^{4+} and U^{5+} in the ordered phase should increase χ by comparison with the high-temperature phase, in which the electrons migrate from ion to ion. The migrating electrons should be characterized by the Pauli component of the susceptibility χ_{Pauli}, which is less by two orders of magnitude than the susceptibility for localized electrons. In fact, the observed $\chi(T)$ curve shows a step with reducing χ on transition to the high-temperature phase. The size of the step enables one to estimate the proportion of the delocalized electron state. The contribution to χ from these electrons is described by Pauli's formula [4]

$$\chi_{\mathrm{Pauli}} = \frac{3N\beta^2}{\varepsilon_F},$$

where ε_F is the Fermi energy; N, Avogadro's number; and β, the Bohr magneton. Substitution shows that χ_{Pauli} is less by about two orders of magnitude than the contributions to χ from electrons localized on the paramagnetic ions. We neglect χ_{Pauli} to get the ratio of the susceptibilities on the two sides of the step:

$$\frac{\chi_l}{\chi_h} = \frac{\mu_1^2 + \mu_2^2}{\mu_1^2(1+x) + \mu_2^2(1-x)}$$

where μ_1 is the magnetic moment of U^{5+} derived here; μ_2 is the magnetic moment of U^{4+} [10]; and x is the proportion of delocalized electrons. The observed ratio is $\chi_\ell/\chi_h = 1.02$. The with $\mu_1 = 2.37$ and $\mu_2 = 3.58$, we get $x = 0.05$, i.e., the unpaired electrons are 5% delocalized in the high-temperature phase.

The Curie–Weiss law applies for $\chi(T)$ above 153 K, with $\mu_{ef} = 2.9\mu_B$ and $\theta = -118$ K.

We can thus say that U_2F_9 has fractional valency only above 6.5 K; at lower temperatures, it can be considered as $UF_4 \cdot UF_5$ and as having a structure close to that of the initial compound U_2F_9. One also assumes that the phase transition causes the electron localization on the U^{4+} and U^{5+} to be ordered, so the symmetry is reduced. As the point-group symmetry of the U_2F_9 molecule is C_2 with an ordered disposition for the U^{4+} and U^{5+} ions, the structure of U_2F_9 at low temperatures can only be of tetragonal symmetry with fourfold axes or a screw 4_2 axis or a mirror-rotation $\bar{4}$ one. As the density should increase on charge ordering, the 4_2 symmetry is probably preferable, in which there is alternation of U^{4+} and U^{5+} along the C_4 axis. With that packing lacking a center of symmetry, the dipole moments of the individual molecules are parallel, which can lead to some macroscopic electrical parameters (piezoelectric or ferroelectric ones).

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^{35}Cl NQR SPECTRA OF COMPLEXES OF TETRACHLOROSTANNANE WITH SUBSTITUTED BENZOYL CHLORIDES

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UDC 548.58+546.814+541.6

^{35}Cl NQR spectra of mixtures of $SnCl_4$ with 2-, 3-, and 4-XC_6H_4COCl were obtained. The electronic and steric structure of the complexes obtained was established. Their formation and structure depend on the nature of substituents X. Complexes with a trigonal-bipyramidal structure are formed with the participation of the carbonyl oxygen atom of the ligand as an electron-donor center, and complexes with trans-octahedral structure, with the participation of the sulfur atom of the X = CH_3S substituent.

In the reaction of $SnCl_4$ with para-substituted benzoyl chlorides, complexes with a 1:1 composition are formed, in which the tin atom is pentacoordinated [1]. We obtained a crystalline complex with this structure in the reaction of ortho-methoxybenzoyl chloride with tetrachlorostannane [2]. In the course of time, it converts into a cis-octahedral complex [2]. In the continuation of a ^{35}Cl NQR study of complexes of tetrachlorostannane with organic ligands, we obtained ^{35}Cl NQR spectra of mixtures of $SnCl_4$ with 2-, 3-, or 4-substituted benzoyl chlorides (Tables 1 and 2).

The NQR spectra of equimolar mixtures of 2-XC_6H_4COCl (X = F, ClCO) and 3-XC_6H_4COCl (X = O_2N, ClCO) consist of the spectra of initial components (Table 1). The same NQR spectra were obtained for these values of X (except for X = F) for mixtures of $SnCl_4$ with 4-XC_6H_4COCl [1]. This indicates the absence of complexation.

A ^{35}Cl NQR spectrum of an equimolar mixture of $SnCl_4$ and 2-ClC_6H_4COCl consists of four lines with different width and intensity. The broad and intense lines in the spectrum are due to superposition of several closely positioned lines. Among these lines, the lowest frequency lies in the same region as most of the spectrum of individual $SnCl_4$. The high-frequency broad and intense line in the spectrum belongs to the chlorine atom in the aromatic ring. The frequency of its maximum (36.88 MHz) practically coincides with that of the line of the same chlorine atom in the individual 2-ClC_6H_4COCl. In the NQR spectrum of a mixture of $SnCl_4$ with 2-ClC_6H_4COCl only one weak single line (29.666 MHz) is observed for the chlorine atom of the COCl grouping. Its frequency practically coincides with that of one of the lines for this chlorine atom in the spectrum of individual 2-ClC_6H_4COCl (see Table 1). The NQR spectrum obtained of a mixture of $SnCl_4$ and 2-ClC_6H_4COCl shows that no complexation took place.

In a quadruplet NQR spectrum of an equimolar mixture of $SnCl_4$ with 2-$CH_3C_6H_4COCl$, the highest frequency line belongs to the chlorine atom in the COCl grouping, and the three low-

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Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Zhurnal Strukturnoi Khimii, Vol. 27, No. 6, pp. 68-72, November-December, 1986. Original article submitted July 30, 1985.

0022-4766/86/2706-0901$12.50