The valence state of uranium in $K_6Cu_{12}U_2S_{15}$

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Abstract

The paramagnetic behavior of $K_6Cu_{12}U_2S_{15}$ has been analyzed, regarding copper as diamagnetic (Cu$^{+}$), sulfur as mixed-valent S$^{\pm}$/S$^{-}$ with magnetically silent delocalized S$^{-}$ holes in the valence band, and the actinide as either U$^{4+}$[5f$^1$] or U$^{5+}$[5f$^0$] in trigonally distorted octahedral surrounding (pseudosymmetry 3m) of sulfur. Fitting procedures have been carried out, accounting for spin-orbit coupling, ligand-field potential (parameters $B_0$), interelectronic repulsion (for U$^{4+}$[5f$^1$]), cooperative magnetic effects (molecular field parameter $\lambda$), and applied magnetic field. Keeping the ratios $B_1/B_0$, $B_2/B_0$, $B_3/B_0$ on their point charge electrostatic values with respect to the sulfur ligands, the three axial parameters $B_k$ ($k = 2, 4, 6$) and $\lambda$ were refined. Agreement between measured and calculated susceptibility data was obtained for U$^{5+}$ with $B_0$ values expected for octahedral surrounding and $\lambda < 0$ speaking for antiferromagnetic interactions. The U$^{5+}$ model does yield a fit of comparable quality, but gives $B_0$ values that are unreasonable with respect to sign and magnitude. To conclude, on the basis of the magnetic properties the title compound is a 5f$^1$ system corresponding to the elements formal charges as either U$^{5+}$ or U$^{5+}$[5f$^0$] and magnetic susceptibilities of finely ground samples have been determined at 0.5 T by SQUID magnetometry (MPMS-5S, Quantum Design) in the temperature range 5–300 K. The data were checked with respect to field dependence at 300 K and found independent of applied field strength $B_0 \leq 1$ T. The experimental data (per U) corrected for diamagnetic contributions are shown in Fig. 1 in the form of the effective Bohr magneton number $\mu_{\text{eff}}$ as a function of $T$. At $T \geq 30 K$, the data are smoothly varying and later used in fitting procedures whereas for $T \leq 30 K$ special features are obvious which may be attributed to magnetic ordering effects [1].

1. Introduction

In $K_6Cu_{12}U_2S_{15}$ (space group Ia3d) mixed-valent S$^{\pm}$/S$^{-}$ with delocalized S$^{-}$ holes in the valence band and metallic conductivity have been observed [1]. Assuming diamagnetic Cu$^{+}$, the actinide can be regarded as U$^{4+}$[5f$^1$] or U$^{5+}$[5f$^0$], corresponding to the distribution of the elements’ formal charges as either (K$^+$(Cu$^{+}$)$_{12}$)(U$^{4+}$(S$^-$)$_2$(S$^{-}$)$_2$)$_2$ or (K$^+$(Cu$^{+}$)$_{12}$)(U$^{5+}$(S$^-$)$_2$(S$^{-}$)$_2$)$_2$. To clarify the valence state of uranium the analysis of the susceptibility data seemed to be promising since the metal (position 16a, site symmetry 3) is coordinated by six sulfur ligands forming a slightly compressed octahedron with high pseudosymmetry 3m.

2. Experimental

Synthesis, crystal structure, electrical and magnetic properties of $K_6Cu_{12}U_2S_{15}$ are described elsewhere [1]. Magnetic susceptibilities of finely ground samples have been determined at 0.5 T by SQUID magnetometry (MPMS-5S, Quantum Design) in the temperature range 5–300 K. The data were checked with respect to field dependence at 300 K and found independent of applied field strength $B_0 \leq 1$ T. The experimental data (per U) corrected for diamagnetic contributions are shown in Fig. 1 in the form of the effective Bohr magneton number $\mu_{\text{eff}}$ as a function of $T$. At $T \geq 30 K$, the data are smoothly varying and later used in fitting procedures whereas for $T \leq 30 K$ special features are obvious which may be attributed to magnetic ordering effects [1].

3. Theoretical

The magnetochemistry of actinides is far from being clarified [2,3]. Since no well defined coupling scheme applies, interelectronic repulsion ($H_{\text{rel}}$), spin-orbit coupling ($H_{\text{SO}}$), and ligand-field potential ($H_{\text{lig}}$) have to be regarded as competing effects acting on the 5f electrons. To accomplish this task, the computer program CONDON has been developed [4,5]. For a 5f$^1$ ion in a ligand field of 3m symmetry, the Hamiltonian reads
3. Results and discussion

Before presenting the results of the fitting procedures, \(\mu_{\text{eff}}\) as a function of \(T\) is given for \(\text{U}^{3+}\) and \(\text{U}^{4+}\) model systems in octahedral coordination serving as a guide for understanding the magnetic properties of \(\text{K}_6\text{Cu}_{12}\text{U}_2\text{S}_{15}\).

\[
\hat{H} = \sum_{\alpha=1}^{N} \left[ -\frac{\hbar^2}{2m_{\alpha}} \nabla^2 \phi_{\alpha} + V(\phi_{\alpha}) \right] + \sum_{\alpha=1}^{N} \frac{\hbar^2}{2m_{\alpha}} \sum_{\beta=1}^{N} \delta(\phi_{\alpha} - \phi_{\beta}) \hat{K}_{\alpha\beta} \delta(\phi_{\alpha} - \phi_{\beta}) + \sum_{\alpha=1}^{N} \mu_{\alpha} (\vec{l}_{\alpha} + 2\vec{k}_{\alpha}) \cdot \vec{B} \right] \]

where \(\hat{H}_L(3\hbar)\) consists of terms \(B^0_{\alpha}C^0_{\alpha}\) with limited number of \(k, q\) given in Eq. (1) [6]. The summation \(i\) is carried out over the number \(N\) of \(f\) electrons. The spherical tensors \(C^0_{\alpha}\) are directly related to the spherical harmonics \(Y^m_l\) \((C^0_{\alpha} = \{4\pi/2\lambda + 1\}^{1/2} Y^{1/2}_l)^{\lambda}\) and the ligand field parameters \(B^0_{\alpha}\) (Wybourne notation) are given by \(A^\lambda_{\alpha}\), where \(A^\lambda_{\alpha}\) is a numerical constant describing the charge distribution in the environment of the metal and \(\phi_{\alpha}\) is the expectation value of \(\phi^\lambda\) for the wavefunction.

The matrix elements of \(\hat{H}\) are evaluated by applying \(\hat{R}_{\alpha\beta} = \hat{R}_{\alpha\beta} = \hat{R}_{\beta\alpha}(3\hbar)\) on the full basis of microstates. Diagonalization leads to the energies \(E_{\alpha}\) and eigenstates \(|\alpha\rangle\), where the latter serve as a basis for the magnetic field effect \(\hat{H}_m = -\mu \cdot \vec{B}\). For specific directions \(u\), the energies \(E_{\alpha,u}\) are calculated and the quantities \(\mu_{\alpha,u} = -\partial E_{\alpha,u}/\partial B_u\) inserted into the general expression of the magnetisation

\[
M_{\text{magn},u} = N_{\text{u}} \sum_{\alpha} \mu_{\alpha,u} \exp(-E_{\alpha,u}/k_B T) \sum_{\alpha} \exp(-E_{\alpha,u}/k_B T).\]

On account of \(\chi_{\text{magn}} = \mu(\mu_{\text{magn},u}/B_u)\) the average susceptibility \(\chi_{\text{magn}} = (x + y + z)/3\) and the effective Bohr magneton number \(\mu_{\text{eff}} = [3k_B/(\mu_{\text{magn}},u)]^{1/2}\) are obtained. Exchange interactions between the magnetic centres are considered in the molecular field approximation \(\chi_{\text{magn}} = \chi_{\text{magn}} - \lambda\), where \(\chi_{\text{magn}}\) is the single-centre susceptibility and \(\lambda\) the molecular field parameter. Positive and negative \(\lambda\) indicates dominant ferromagnetic and antiferromagnetic interactions, respectively, between the uranium ions.

4.1. Simulation calculations for \(\text{U}^{3+}\) and \(\text{U}^{4+}\) in octahedral surrounding

The ligand-field parameter for the one-electron system \(\text{U}^{3+}\) in a ligand field of cubic symmetry with reference to the three-fold axis [7] is given by

\[
\hat{H}_L(\text{cub}) = \hat{B} \left[ C_3^g - \sqrt{\frac{6}{7}} (C_2^g - C_2^e) \right] + \hat{B} \left[ C_6^g + \frac{\sqrt{15\Gamma_7}}{24} (C_6^g - C_6^e) \right] + \frac{\sqrt{3\Gamma_7}}{24} \left[ C_2^g + C_2^e \right].\]

Assuming a reasonable total splitting of \(\approx 9000\text{ cm}^{-1}\) for the free ion ground state \(2F\) by \(\hat{H}_L(\text{cub})\), the ligand-field parameters \(B_0^g = -4200\text{ cm}^{-1}\) and \(B_0^e = 1560\text{ cm}^{-1}\) have been estimated [8], while \(\zeta\), deduced from spectroscopic investigations of \(\text{U}^{3+}\) compounds, was set to 1820 cm\(^{-1}\) [9]. With respect to the \(5f^2\) system of \(\text{U}^{4+}\), the corresponding parameters \(B_0^g = -5520\text{ cm}^{-1}\) and \(B_0^e = 2040\text{ cm}^{-1}\) have been
The signs of the refined quality is obtained (Fig. 1, (—)) with parameter values given in the third column of Table 1. The slight loss of quality. However, in any case the general pattern correlation further adaptations were obtained with only minor changes. The application of a molecular-field parameter is essential for a good fit. To conclude, the experimental data were nicely simulated with the Slater–Condon parameters. As distinguished from the 5f\(^1\) system of pentavalent uranium, the tetravalent system with 5f\(^2\) demands the consideration of the interelectronic repulsion. The magnetic behaviour of the two centres, presented in Fig. 1, resembles the solid line (—) in Fig. 2 for U\(^{4+}\), the latter keeping at 1820 cm\(^{-1}\). While for U\(^{5+}\) the ground state (\(\Psi_0\)) is magnetic (slightly decreases in U\(^{4+}\)) with decreasing \(T\), the decrease of \(\mu_B U\) \(\sim \sqrt{T} \rightarrow 0\) for U\(^{4+}\) corresponds to temperature-independent paramagnetism (TIP) according to a singlet ground state (\(\Psi_0\)). The solid lines (—) demonstrate the influence of antiferromagnetic U–U interactions described by \(\lambda = -0.7 \times 10^2\) mol \(^{-1}\) (SI units).

As matters stand at present, the low-temperature measured data (Curie paramagnetism instead of TIP) speak for pentavalent uranium in the compound under investigation.

### 4.2. Fitting procedures assuming U\(^{4+}\)

The general feature of the experimental \(\mu_B\) curve (see Fig. 1) resembles the solid line (—) in Fig. 2 for U\(^{4+}\), i.e., for a successful adaptation antiferromagnetic interactions have to be considered. The application of \(\hat{H} = \hat{H}_\text{int} + \hat{H}_\text{q} + \hat{H}_\text{q} (3\mu)\) of Eq. (1) on the 14 microstates \(|\mu,\mu\rangle\) gives rise to a splitting into seven Kramers doublets where the energy differences are given by six ligand-field parameters \(R_b\) and the spin-orbit coupling parameter \(\xi\), the latter keeping at 1820 cm\(^{-1}\) as before. Since it is impossible to derive the set of six \(R_b\) parameters from susceptibility data, we reduced their number according to current practice [6] by keeping the ratios \(\langle 1/2,1/2\rangle/\langle 1/2,-1/2\rangle\) on their point charge electrostatic (PCE) values with respect to the nearest-neighbour polyhedron (see Table 1, second column).

Refining \(R_b\) (\(k = 2, 4, 6\)) and \(\xi\), an adaptation of high quality is obtained (Fig. 1, (—)) with parameter values given in the third column of Table 1. The signs of the refined \(R_b\) are in agreement with the PCEM data. Owing to parameter correlation further adaptations were obtained with only slight loss of quality. However, in any case the general pattern correlation further adaptations were obtained with only slight loss of quality. However, in any case the general pattern correlation further adaptations were obtained with only slight loss of quality. However, in any case the general pattern correlation further adaptations were obtained with only slight loss of quality.
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References

[5] PROGRAM CONDON is free software, covered by the GNU General Public Licence, and is available from http://www.condon.fh-aachen.de.