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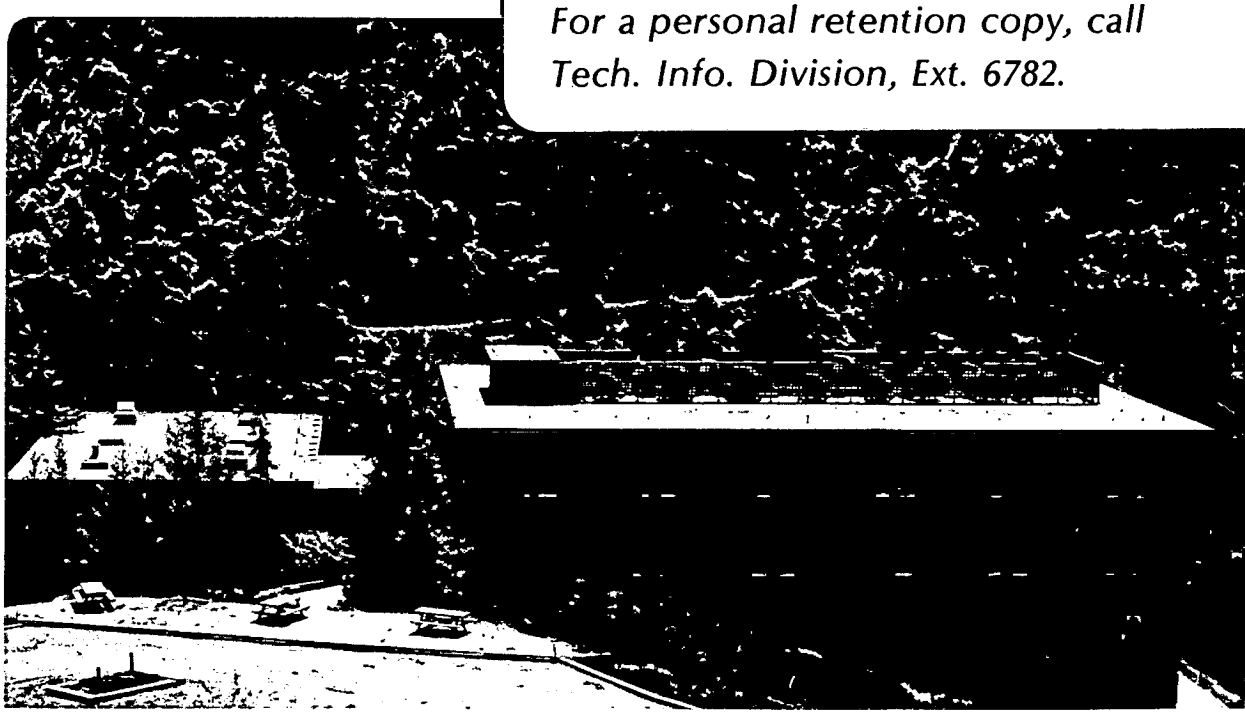

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Anisotropic Magnetic Susceptibility of Single Crystal UCl_4

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Abstract

The anisotropic magnetic susceptibilities $\chi_{\parallel}$ and $\chi_{\perp}$ of UCl_4 have been measured in single crystals between 1.6 and 350 K. Powder measurements of the average susceptibility were also performed but were found to be unreliable due to orientation effects. The single crystal results were interpreted in terms of the parameterized crystal field model with the following parameters $\zeta = 1819\ cm^{-1}$, $F^2 = 42632\ cm^{-1}$, $F^4 = 38680\ cm^{-1}$, $F^6 = 23320\ cm^{-1}$, $B_0^2 = -1008\ cm^{-1}$, $B_0^4 = 1730\ cm^{-1}$, $B_4^4 = -2704\ cm^{-1}$, $B_0^6 = -2705\ cm^{-1}$, $B_4^6 = 346\ cm^{-1}$, $\alpha = 29\ cm^{-1}$, $\beta = -638\ cm^{-1}$ and $\gamma = 1671\ cm^{-1}$. These parameters yield a $\Gamma_4(^3H_4)$ ground state and a paramagnetic first excited state $\Gamma_5(^3H_4)$ at 110 cm^{-1} and are in good agreement with the optical spectrum.

Introduction

Measurements of the magnetic susceptibility of UCl_4 powders have been carried out by several different groups of investigators over the past 30 years.[1-4] Attempts to calculate the susceptibility from wave functions based on a crystal field analysis of the optical data have also been undertaken[5] but failed to reproduce the optical spectrum and the magnetic behavior in a satisfying way. This might have been caused partly by the fact that the interpretation of the optical spectrum has not yet been definitively resolved.[5,6]

Measurements of susceptibilities, especially in single crystals can be a sensitive tool to check on the eigenvectors and energies of thermally populated states. The purpose of this paper is to present magnetic susceptibility data for UCl_4 single crystals between 1.8 and 350 K and their interpretation in terms of wavefunctions obtained from a parameterized ligand field analysis of the optical spectrum.

Experimental Details

The synthesis of UCl_4 and the growth of single crystals have been described elsewhere.[7] The susceptibility measurements were carried out on a SHE 905 SQUID Magnetometer. The samples were weighed and sealed into previously calibrated containers in an inert atmosphere box. Weights of the single crystals ranged from 18 to 40 mg. Several powdered samples were also examined as a cross reference with their weights ranging from 200 to 400 mg. Several runs with different samples and containers were made to check for

reproducibility. The single crystals were mounted inside the containers with their crystallographic c-axis either parallel ($\chi_{\parallel}$) or perpendicular ($\chi_{\perp}$) to the magnetic field. Applied fields were between 0.5 and 40 kGauss, temperatures ranged from 1.6 to 370 K. The suceptibility in these ranges was not significantly field dependent.

Results

The most recent optical analysis[6] of solid UCl_4 (molecular symmetry D_{2d} [8]) predicts a nonmagnetic Γ_4 ground state and a paramagnetic Γ_5 state about 120 cm^{-1} above it (Parameter set A in Table 2). This implies a very anisotropic susceptibility with $\chi_{\parallel}$ expected to be about 30 times smaller than $\chi_{\perp}$. A crystallite of a substance with such an anisotropic susceptibility tensor tends to reorient in a static homogenous magnetic field with the axis of greatest susceptibility parallel to the field.[9] The effect is stronger at low temperatures and of course depends on the magnitude of the applied magnetic field. Because of this we found it almost impossible to obtain reliable powder data for UCl_4 at temperatures below 20 K even with a field as small as 0.5 kGauss. The powder reoriented slowly and the measured susceptibility increased with time until it reached the value of $\chi_{\perp}$ measured in the single crystal. This effect could be reduced somewhat by thoroughly packing the sample, but could not be totally eliminated. The lack of reproducibility in earlier measurements of the powder susceptibility of UCl_4[1-4,10] might be due to this reorientation effect.

The following analysis was therefore based solely on single crystal data. Representative values of experimental susceptibilities $\chi_{\parallel}$ and $\chi_{\perp}$ are listed in Table 1. An isotropic diamagnetic correction of -139×10^{-6} cgsu/mol was applied. Experimental values are plotted as a function of temperature in Figure 1. The error bars indicated in Fig. 1 were estimated from repeated runs with different crystals. They are considerably larger for $\chi_{\parallel}$ than for $\chi_{\perp}$ because of orientation difficulties.

$\chi_{\parallel}$ was not found to be significantly temperature dependent, the average over the whole temperature range being $(11.8 \pm 0.9) \times 10^{-4}$ cgsu/mol. Between 1.6 and 15 K, $\chi_{\perp}$ is temperature independent and then increases slightly but significantly to 2.19×10^{-2} cgsu/mol at 25 K. At higher temperatures, $\chi_{\perp}$ shows Curie Weiss behaviour $[\chi = C/(T-\theta)]$ as shown by the plot of $\chi_{\perp}^{-1}$ vs. T in Figure 2. Linear regression of $\chi_{\perp}^{-1}$ vs. T above 60 K yielded a Weiss constant $\theta_{\perp} = -28.8$ K and a Curie constant $C_{\perp} = 1.726$. The average effective magnetic moment $\mu_{\perp}$(eff) from this regression was found to be 3.72 ± 0.02 Bohr Magnetons. A plot of the uncorrected effective moment $\mu_{\perp}$(eff) vs. temperature is shown in Figure 3.

Analysis and Discussion

The electronic states resulting from an f^2 configuration restricted to D_{2d} symmetry can be described with an effective Hamiltonian of the form[11]

$$H = H_1 + H_2 + H_3 + H_4 \tag{1}$$

where

$$H_1 = F_o + \sum_{k=2,4,6} F^k(5f,5f) \sum_{i>j=1}^{n} c_i^k \cdot c_j^k \,, \tag{2}$$

$$H_2 = \sum_{i=1}^{n} \zeta_{5f} \, \vec{\ell}_i \cdot \vec{s}_i \tag{3}$$

$$H_3 = B_o^2 C_o^2 + B_o^4 C_o^4 + B_4^4 (C_4^4 + C_{-4}^4) + \tag{4}$$

$$+ B_o^6 C_o^6 + B_4^6 (C_4^6 + C_{-4}^6)$$

$$H_4 = \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) + \cdots, \tag{5}$$

where $G(G_2)$ and $G(R_7)$ are representations of Casimirs operator for the groups G_2 and R_7 on the appropriate manifold. In addition, H_4 contains terms parameterizing magnetic interactions (M^k, P^k)[11,12] which were omitted in this analysis.

The 13 parameters explicitly contained in Eqs. (2)-(5) can be adjusted to give the best fit to experimental energy levels obtained from optical spectroscopy. Different interpretations of the spectrum of UCl_4 have been published,[6,13] using quite different assignments of the transitions and yielding different parameter sets (see Table 2). Using the full basis of 70 eigenfunctions of the f^2 configuration obtained from the parameter sets of Hecht and Gruber[13] (denoted B in Table 2) and C. Khan Malek[6] (set A), we calculated the susceptibility along the z-axis ($\chi_{\parallel}$) and x-axis ($\chi_{\perp}$). The calculated values are also shown in Figure 1.

While set B reproduces the low temperature part of $\chi_\perp$ very poorly, set A is in fairly good agreement with the experiment. The failure of set B to reproduce the low temperature susceptibility is mainly due to the position of Γ_5 ($^3H_4$) at 212 cm^{-1}, which is obviously too high, thus giving susceptibilities which are too small at low temperatures. Hecht and Gruber tried to compensate for this fact by adjusting their value of B_4^6 to get a good fit for the susceptibility, finding $\Gamma_5(^3H_4)$ at 110 cm^{-1} above the ground state Γ_4. This results in an excellent fit of $\chi_\perp$ but a very bad fit of their optical data (Parameter set C in Table 2).

Attempts to fit the parameters of the Hamiltonian (1) to the susceptibility alone are not very useful, because the fit depends mainly on the relative energies of the lowest lying, thermally populated levels. Several, almost identically good fits as with set A could be obtained with very different values for the crystal field parameters. But these in turn would not satisfactorily reproduce the optical spectrum. Even if the basis set was reduced to the 9 crystal field states originating from the free ion ground term $^3H_4$ alone, a good fit was obtained. As long as $\Gamma_4(^3H_4)$ is the ground state, $\Gamma_5(^3H_4)$ about 110 cm^{-1} above it and no other magnetic state is thermally populated, almost any choice of parameters and basis set reproduces the susceptibility fairly well.

After adding the proposed level Γ_5 at 110 cm^{-1} to the 17 optical assignments given by C. Khan Malek,[6] the fitting of the optical data was repeated, starting with parameter set A. This

resulted in the slightly different set D, which gave an equally good fit to the optical data but increased the goodness of the susceptibility fit considerably as shown in Figure 1 and the standard deviations in Table 2. The calculated values for $\chi_{\perp}^{-1}$ and $\mu_{\perp}$(eff) with set D are plotted in Figures 2 and 3, showing good agreement at low temperatures. The deviations at higher temperature cannot be explained. They could be due to orbital reduction caused by covalency. Only a very small adjustment to the crystal field parameters would be necessary to correct for the deviations, but this does not seem useful as long as the optical analysis, which must be the basis for any parameter set, does not reproduce the optical data more satisfactorily.

Conclusions

The calculated single crystal susceptibilities of UCl_4 are in fair agreement with experiment, the fit being poorest at high temperatures for $\chi_{\perp}$. This fit could easily be improved with only minor changes in the crystal field parameter set or by the introduction of orbital reduction factors into the Hamiltonian. However it would be more desirable to have a better parameter set based on an improved fit to the optical data, rather than relying on a fit to the susceptibility data which is very sensitive only to the low lying crystal field levels.

The work presented here shows also the importance of single crystal susceptibility measurements for actinide compounds with low

symmetries and nonmagnetic ground states. Powders alone yield only limited information which might even be erroneous due to reorientaton effects if the X-tensor is very anisotropic.

Acknowledgements

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Table 1. Magnetic Susceptibilities in $UCl_4(s)$

T (K)	$\chi_{\parallel}$ (10^{-2} cgsu/mol)	$\chi_{\perp}$ (10^{-2} cgsu/mol)	$\bar{\chi}$ a) (10^{-2} gcsu/mol)
1.66–15.0	0.130	2.165	1.487
20	0.129	2.180	1.496
25	0.130	2.192	1.505
30	0.130	2.191	1.504
35	0.129	2.169	1.489
40	0.128	2.127	1.461
60	0.124	1.853	1.277
80	0.121	1.573	1.089
99	0.118	1.346	.937
120	0.117	1.166	.816
140	0.115	1.103	.774
160	0.114	0.924	.654
199	0.110	0.836	.594
219	0.109	0.763	.544
238	0.109	0.651	.476
258	0.110	0.601	.437
277	0.110	0.562	.411
300	0.110	0.519	.383
350	0.107	–	–

a) $\bar{\chi} = (\chi_{\parallel} + 2\chi_{\perp})/3$, average susceptibility

Table 2. Parameter Sets and Crystal Field Splitting of the Ground State Level $^3H_4$ of UCl_4 (s) (in cm^{-1})

Parameter[a] Set	A	B	C	D
	1819(23)	1666(11)	...[b]	1819(10)
F_0	11728(1190)	–	–	–
F_2	42525(1110)	38835(400)	...	42632(750)
F_4	38600(1970)	42242(1200)	...	38680(1630)
F_6	23082(2630)	18846(720)	...	23320(2010)
B_0^2	-992(265)	-583(160)	...	-1008(198)
B_0^4	1625(683)	-3027(238)	...	1730(362)
B_4^4	-2722(250)	-5679(175)	...	-2704(193)
B_0^6	-2852(1114)	-2262(432)	...	-2705(665)
B_4^6	406(510)	795(249)	2226	346(436)
α	29(4)	–	–	29.4(3)
β	-629(264)	–	–	-638(170)
γ	1765(935)	–	–	1671(663)
Energies in the $^3H_4$ manifold	0[c] Γ_4	0 Γ_4	0 Γ_4	0 Γ_4
	119.2 Γ_1	211.6 Γ_5	110.3 Γ_5	97.2 Γ_1
	120.9 Γ_5	535.9 Γ_1	357.8 Γ_1	109.1 Γ_5
	702.9 Γ_2	1460.3 Γ_3	1338.2 Γ_3	687.7 Γ_2
	867.2 Γ_3	16356 Γ_2	1576.6 Γ_2	844.4 Γ_1
	871.9 Γ_1	1878.1 Γ_5	1792.8 Γ_5	873.0 Γ_3
	1114.8 Γ_5	2255.1 Γ_1	2358.3 Γ_1	1112.9 Γ_5
$n(E)$[d]	17	36	36	18
$\sigma(E)$[e]	33	89	138	32
$\sigma(\chi_{\parallel})$[f]	$.53\times10^{-3}$	$.48\times10^{-3}$	$.85\times10^{-3}$	$.58\times10^{-3}$
$\sigma(\chi_{\perp})$[f]	1.42×10^{-3}	6.13×10^{-3}	$.43\times10^{-3}$	1.28×10^{-3}
$\sigma(\bar{\chi})$[f]	1.00×10^{-3}	3.94×10^{-3}	$.71\times10^{-3}$	$.91\times10^{-3}$

Footnotes for Table 2.

[a] Origin of parameter sets:

A: Khan Malek,[6] optical analysis
B: Hecht and Gruber,[12] optical analysis
C: Hecht and Gruber,[5] vary B_4^6 to fit susceptibility
D: This work, optical data from [6] plus $\Gamma_5(^3H_4) = 110\ cm^{-1}$

[b] All parameters except B_4^6 as in set B

[c] All energies shifted by +15.6 cm^{-1} so that the ground state is at 0 cm^{-1}

[d] n(E): number of optical assignments

[e] Energy standard deviation in optical fit (cm^{-1})

[f] Standard deviations in susceptibility fits (cgsu/mol)

$\sigma(\chi_{\parallel})$: data for $\chi_{\parallel}$ alone
$\sigma(\chi_{\perp})$: data for $\chi_{\perp}$ alone
$\sigma(\bar{\chi})$: all experimental data

Figure captions

Figure 1. Molar single crystal susceptibility in UCl_4 as a function of temperature. Diamagnetic correction: $\chi_{dia} = -139 \times 10^{-6}$ cgsu/mol^{-1}. The labels of the calculated curves correspond to those in Table 2.

Figure 2. Inverse single crystal susceptibility in the (001)-plane ($\chi_\perp$) in UCl_4 as a function of temperature. The solid line was calculated from parameter set D in Table 2.

Figure 3. Effective magnetic moment in the (001)-plane ($\mu_\perp$(eff)) in UCl_4 as a function of temperature. The solid line was calculated from parameter set D in Table 2.

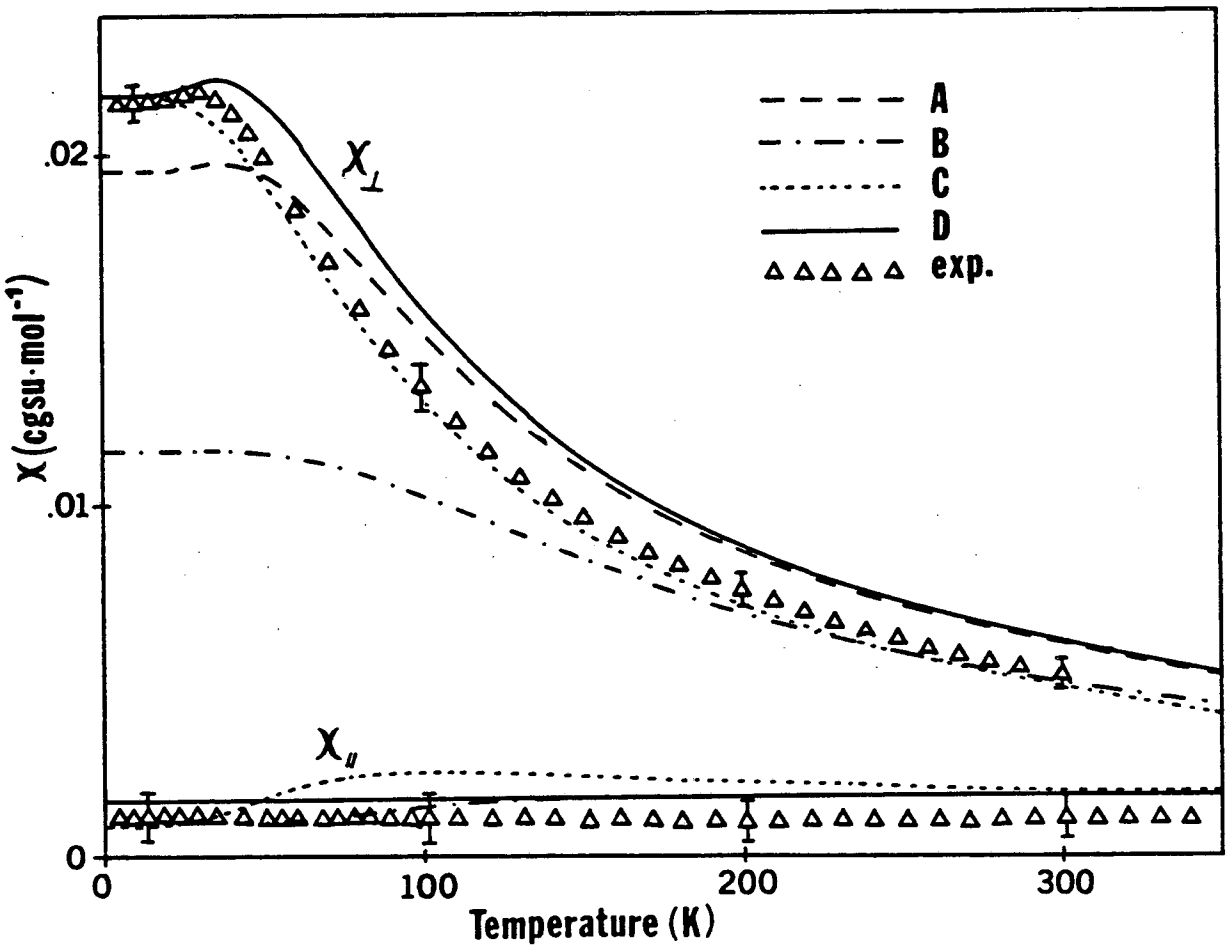

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Figure 1

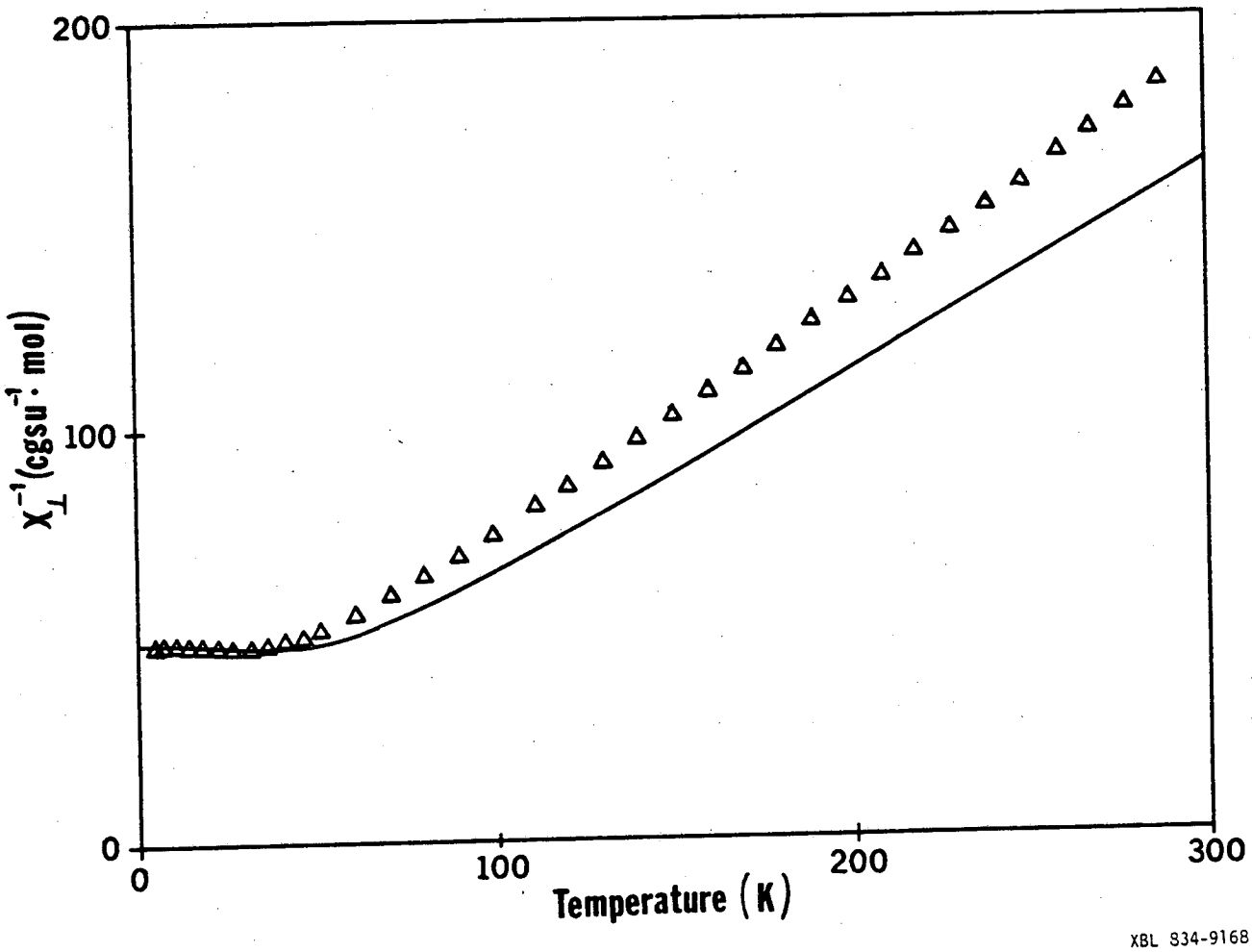
200
100
0
0
100
200
300
$\chi_{\perp}^{-1}$(cgsu^{-1} · mol)
Temperature (K)
XBL 834-9168

Figure 2

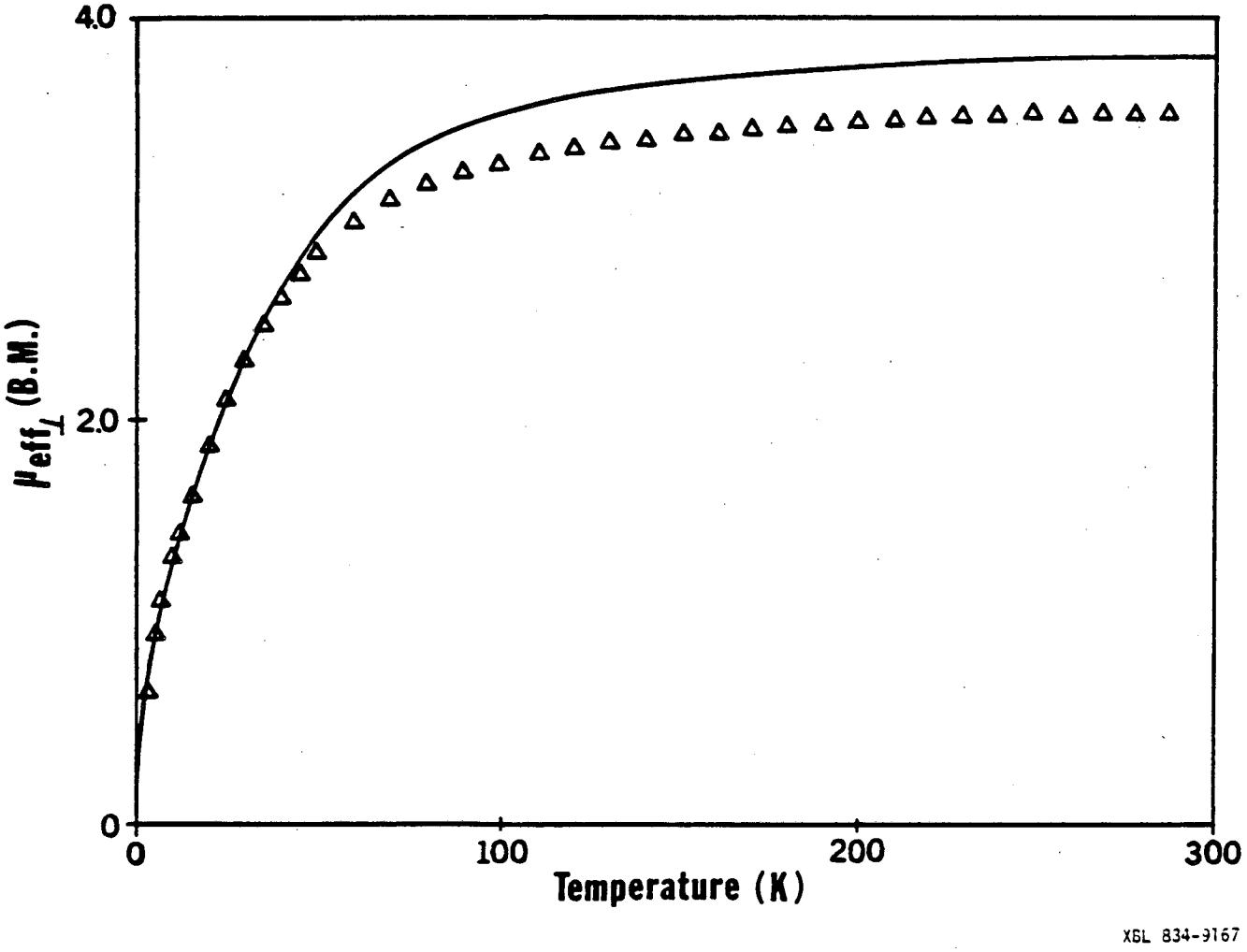

Figure 3

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