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Abstract

First, we review earlier studies reporting possible magnetic characteristics for radiation defects in Pu. We then report, for α-Pu, two studies of the excess magnetic susceptibility (EMS) due to radiation damage, as a function of time and temperature. We have observed several annealing stages associated with the EMS of the accumulated self-damage and we report that annealing begins at ~31K, while below that temperature the displacement damage from self-irradiation of the Pu alpha particle emission and the U recoil are immobile. A detailed investigation was made of this EMS well below the first annealing stage as a function of temperature (2K<T<15K) and time in a magnetic field of 2T. A linear increase in magnetic susceptibility is seen as a function of time for all isotherms. The excess susceptibility per alpha decay, determined from a linear fit of the slope of the time dependent EMS, is reasonably described with a Curie-Weiss law exhibiting a small negative Weiss temperature. We conclude by describing some future experiments in light of the present results.

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I. Introduction

Plutonium's unusual position in the actinide series places it directly between the light actinides with ***f***-electron delocalization, and the heavy actinides with ***f***-electron localization. Point- and extended-defects are expected to, and do exhibit extraordinary properties as a consequence of the unusual nature of plutonium's electronic structure. The first to notice and report an associated excess magnetic susceptibility (EMS) from radiation damage was Dormeval[1]. Figure 1 shows the low temperature deviation of the magnetic susceptibility due to radiation damage from the alpha decay of Pu and Am in several $Pu_{1-x}(Am_x)$ alloys where each alloy has been aged at room temperature such that the same amount of displacement damage is accumulated. It is reported that when the magnetic susceptibility of these specimens was examined at a magnetic field of 2T, an anomaly was seen below 75K as illustrated in Figure 1. This anomaly, or EMS, does not manifest at higher fields, and permanently disappears upon annealing for sufficient time at 450C.

Recently, we reported that vacancies and vacancy clusters in Pu(3.3 at% Ga) ***fcc*** δ-phase behave in an anomalous manner with respect to their specific resistance[2]. The specific resistance of three defect populations is shown in Figure 2; the upper curve is a mixture of vacancies and interstitials; the two lower curves are the temperature dependent resistance of what is primarily vacancy and vacancy cluster defect populations, each of the two vacancy dominated defect populations having been synthesized through annealing at 150K and 250K following several days of accumulated radiation damage. The vacancy defect resistance follows a ***–ln(T)*** behavior from 250K to 10K, suggesting the possibility of local moments or Kondo-like impurity behavior in the phonon sensitive regime above the Kondo temperature (estimated <10K).

As a third example of "tunable" magnetic effects in Pu, we turn again to the thesis of Dormeval[1], where the measured magnetic susceptibility as a function of Am concentration was determined for a suite of $Pu_{1-x}Am_x$ alloys, with x=0.049 to 0.43. By using a modified Curie-Weiss analysis according to the relation;

$$\chi = \chi_0 + \frac{C}{T - \theta_p} \text{ and } \mu_{eff} \approx \sqrt{8C} \qquad (1)$$

where χ is reported in emu/mole and the effective moment, μ_{eff} in Bohr magnetons, was deduced, and plotted as shown in Figure 3. Dormeval interpreted the step like behavior as indicative of a transition from a low Am concentration regime, where Kondo shielding is operative, to a higher concentration regime, of increased ***f***-electron localization. A somewhat analogous result has been reported by Griveau and co-workers[3], where a localization to delocalization transition is suggested for Am under increasing pressure.

The three examples cited above all point to the extraordinary sensitivity of Pu to any type of perturbation, radiation defects for the first and second examples, and lattice expansion effects of alloying with a neighboring closed shell actinide for the third. The experimental work described below sets out to explore the evolution of magnetic properties in radiation damaged α-Pu through the study of magnetic susceptibility as a function of time and temperature. We note that Pu exhibits no clear evidence for collective magnetism at accessible temperatures, having been recently reviewed[4], despite having an anomalously large magnetic susceptibility in all its various phases.

II. Sample Preparation

An α-Pu (99.98% pure) specimen which was 2 years since having been melted and electro-refined, was mechanically shaped to 1x2x2mm, then mechanically and chemically cleaned of oxide, yielding a specimen of 56.8mg (Figure 4). The majority of the sample is ^{239}Pu (93.7%), with smaller concentrations of ^{240}Pu (5.86%) and ^{238}Pu (0.17%) contributing appreciably to the activity of the sample. The balance of the specimen included the following magnetic impurities: Fe(54ppm), Ni(6ppm), Cr(2.7ppm) and Mn(2.4ppm). The specimen was coated with ~5 microns of polyimide which was cured at 350K (below the α to β Pu phase transformation) for several hours. The specimen was mounted in a well characterized cartridge-brass alloy tube (20cm long) (Figure 4), hermetically sealed under an atmosphere of helium and measured using a commercial magnetometer (Quantum Design MPMS-5) where the small background contribution of the tube could be readily subtracted from the raw data. It was determined that the EMS, which was observed to accumulate at low temperature, could be annealed at 350K. Two experiments are reported here;

- A radiation damage accumulation and subsequent isochronal annealing experiment

- An aging study as a function of time and temperature, carried out below Stage I (the temperature below which the defects are immobile).

III. Isochronal Annealing of α-Pu Specimen

In this experiment we accumulated radiation damage for 51 days below 15K. Then an isochronal annealing study was performed where the annealing protocol was to ramp up to the annealing temperature at 12K/min, hold for 30 min., and ramp down to 5K at 12K/min., with the total annealing process taking 6 days. An experimental correction was made for damage accumulated during the annealing protocol. This correction protocol is described in reference 2.

The annealing data for the accumulated EMS is shown in Figure 5 as the open squares. A comparison is shown to an annealing study of α-Pu (filled circles) made by Wigley[5] using the more common method of resistance measurements. While the comparison is qualitatively similar we note that differences in specimen chemistry, and the length of the damage accumulation period will contribute to differences in the two annealing curves. The present data is of very good fidelity and allows us to identify that below 31K the accumulated defects are indeed immobile. However, notice that the data below ~20K exhibits a small positive slope which may be due to the exact physical nature of the EMS. Future work should allow a more complete understanding of this detail. We also note, that 315K is a good estimate of the temperature above which all the accumulated damage is fully annealed. This later observation, however, should be qualified, as we know that helium and radio-decay impurities are neither annealed nor removed from the system at such a low temperature.

IV. Time and Temperature Behaviour of Accumulating Excess Magnetic Susceptibility

We have a fortuitous opportunity to study the time and temperature properties of the EMS below the Stage I annealing temperature where the defects are immobile. The experiment shown in Figure 6 shows the time evolution of the EMS for 2K<T<15K. The inset in Figure 6 is an experimental determination of the magnetic susceptibility, $\chi(\boldsymbol{T},\boldsymbol{t}=0)$, for a freshly annealed (t=0) specimen where the low temperature upturn in χ is almost entirely attributable to Fe impurities (~50ppm determined by inductively coupled plasma mass spectrometry). After annealing and maintaining the specimen below T=15K for an elapsed time of ~27 days, the EMS was followed as described above. The data was recorded at $\mu_0 H$=2T according to the following temperature protocol: For 5K ≤ T ≤ 15K: {Measure at T, Measure at 5K, Increment T by 0.5K} with this sequence of temperatures repeated for 12500 minutes. The measurement at each temperature is an average of ~20 data points taken over the course of ~45 minutes to ensure temperature stability. Later, a similar sequence, cycling between 2K and 7K was repeated 10 times over the course of ~6000 minutes with the 5K isotherm in common with the two data sets.

We would expect that the intercept, $\chi(T, t=0)$, of the isotherms in Figure 6 should be identical to the annealed susceptibility. On inspection we note that the linear extrapolations of the isotherms to ***t***=0 are systematically high relative to the measured $\chi(T, t=0)$ in the inset, indicating a possible curvature, requiring further study. The slopes of the various isotherms are simply $d(\Delta\chi(T,t))/d\boldsymbol{t}$. The simple relationship governing temperature and time evolution of the EMS for the purpose of this report is thus given by;

$$\chi(T,t) = \chi(T, t=0) + \Delta\chi(T,t) \tag{2}$$

A study of the defect EMS offers the opportunity to examine the response of the α-Pu to the presence of disorder. In a very real sense, disorder can serve as a local perturbative probe of a complex highly correlated electron system. Here, we report the apparent interaction among the defects contributing to the EMS. This is done by inspecting the Curie-Weiss relationship as applied to the data in Figure 5,

$$\left(\frac{dt}{d(\Delta\chi)}\right)\left(\frac{d\alpha}{dt}\right) = \frac{T-\theta_p}{C} \tag{3}$$

where, $d\boldsymbol{t}/d\Delta\chi$ is the reciprocal of the change in the EMS per time, simply the reciprocal of the slope of the isotherms, which, is independent of the ***t***=0 intercept in equation 2, and dα/dt is the number of alpha decays per mole of Pu per unit time determined from the measured isotopics. The Curie-Weiss plot in Figure 7 is the reciprocal of the susceptibility per alpha decay, derived from the slopes in Figure 6, where we have converted time into alpha decays according to the left side of equation 3. The line is the best fit to equation 3 with the goodness of fit 0.99638. We note that there is a hint of curvature in the data suggesting the need for experiments at higher temperatures. A small negative Weiss temperature slightly larger than 5K is noted suggesting weak antiferromagnetic interactions, possibly alluding to frustrated or glassy behavior or an indication of Kondo behavior with T_K ~ 1-2K.

V. Discussion and Future Work

As illustrated by the earlier examples and the present results, radiation damage induced EMS appears to be extant in both α-Pu and alloy "stabilized" δ-Pu using Ga or Am as the alloying element. Given the similarities in the spectroscopic properties and the close lying energy levels of the α- and δ-Pu ground states, this is not so surprising. This point has been noted in recent theoretical work of Savrasov and co-workers [6], which have provided evidence that the alpha and delta phases are not fundamentally different; perhaps in a way similar to the suggestion of Chapline and co-workers[7] that the alpha and gamma phases of cerium are similar. We observe, in passing, that the change in thermal expansion of δ-Pu with doping is analogous to the quantum critical behavior of heavy fermion alloys near where magnetic ordering vanishes: and may be related to a proximity to magnetic ordering in plutonium and its simple alloys.

The anomalous properties of radiation induced defects in α-Pu may allow us to infer that α-Pu is near to a different phase with some kind of hidden quantum order. From the Curie-Weiss analysis of Figure 7, an effective moment of $550\mu_B/\alpha$ decay may be extracted. This moment arises from the defects (vacancies and interstitials, and their aggregates such as loops, and clusters) created by the alpha decay and U recoil, where some 300-1000 vacancy-interstitial pairs are expected to survive per alpha event, with the majority of the surviving defects expected to cluster near the region of the ~2700 initial defects from the U displacement cascade. As these defect clusters accumulate with time, they should begin to interact, both indirectly by distorting the local electronic structure, and directly as the cascade volumes begin to physically overlap. This interaction should manifest itself in the evolving EMS as a deviation from the simple linear time dependence applied here.

Future experiments will aim at identifying the nature of the quantum order associated with the EMS in a variety of Pu alloys by following the evolving physical properties over a wider time and temperature regime. It is worth noting that the abrupt change in deduced effective moment for the alloy $Pu_{1-x}Am_x$ for x near to 0.25 reported in reference 1, may correspond to one of the phase transitions in reference 3 for Am under pressure. The question as to whether these transitions are related to our EMS warrants further investigation.

Acknoledgements

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Figure Captions

Figure 1: The excess magnetic susceptibility for "aged" PuAm binary alloys as described in the text. ***from reference*** 1.

Figure 2: The resistance, ***R,*** for the three defect populations resulting from self-irradiation (SI) of δ-Pu(Ga) at 10K for 5 days. The inset shows the data (magnified) for the two vacancy dominated defect populations arising from the annealing at 150K and 250K. A ***possible, but unproven*** interpretation of the observed –***ln***(T) behavior, is a Kondo-like nature for vacancies in Pu(Ga) with a Kondo temperature, T_K<10K. ***from reference*** 2.

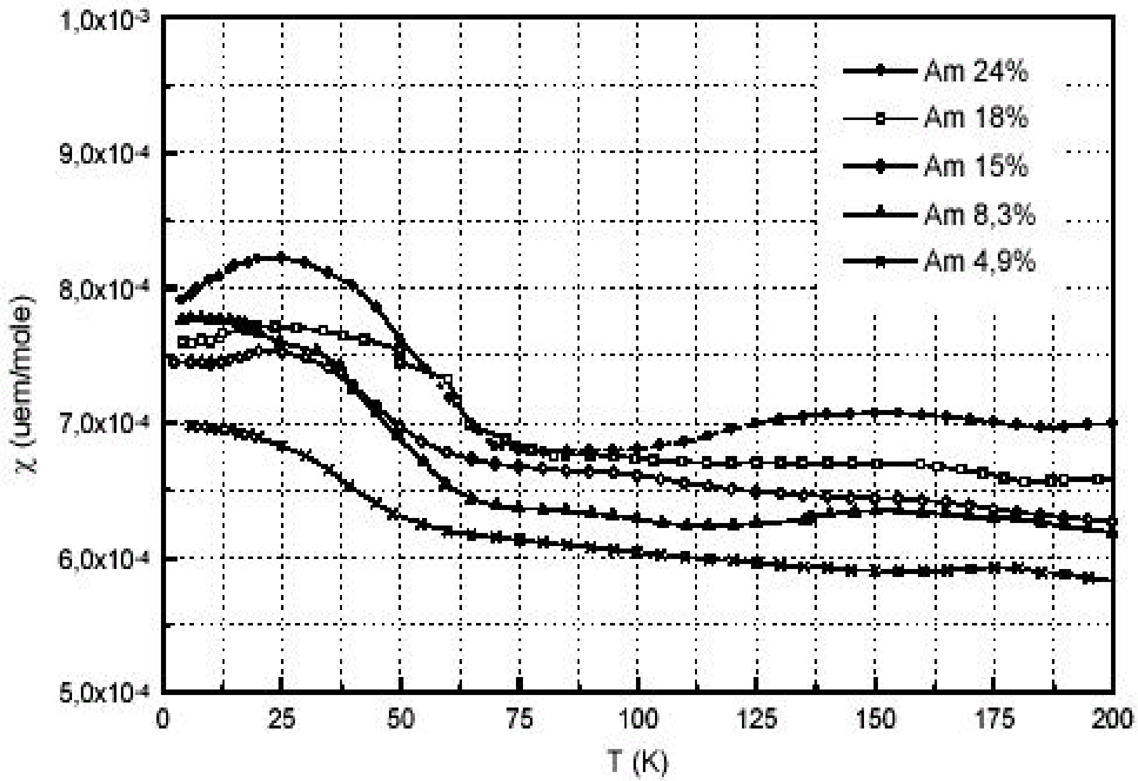
Figure 3: Parameters deduced from a Curie-Weiss law analysis according to the americium content. The lines are guides for the eyes and indicate the trend near 25 %Am. ***from reference*** 1.

Figure 4: Alpha-Pu specimen and cartridge brass holder.

Figure 5: The α-Pu annealing curve of the EMS in this work is shown as open circles. For comparison, the resistivity annealing data is shown from the work of Wigley (reference 5). The line is a guide the eye. Our EMS data indicates defect immobility below ~31K and full annealing at 315K.

Figure 6: The measured time and temperature behavior of the accumulating EMS is illustrated. The data at half integer temperatures has been left out of the illustration for clarity. Note, that the measurements were taken starting ~33,000 minutes after annealing. Two sets of data taken at different times are indicated, the earlier from 5K to 15K and later from 2K to 5K. The consistency of the 5K data allows us to treat this as a single data set. The temperature dependence of the susceptibility of the annealed specimen is shown in the inset.

Figure 7: A Curie-Weiss plot of the reciprocal of the magnetic susceptibility per alpha decay. The data points are vertical lines indicating the statistical errors associated with each point. The fit to equation 3 is reasonable (goodness of fit 0.99638) but a noticeable deviation is evident at the higher temperatures.



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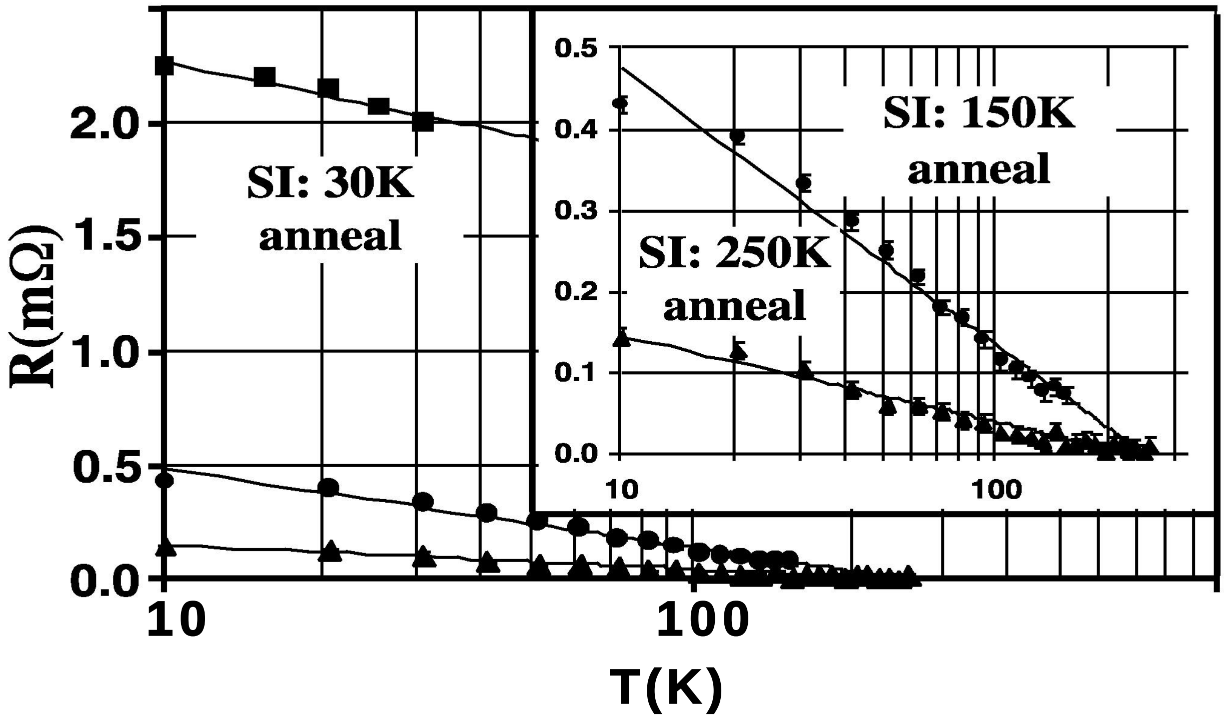

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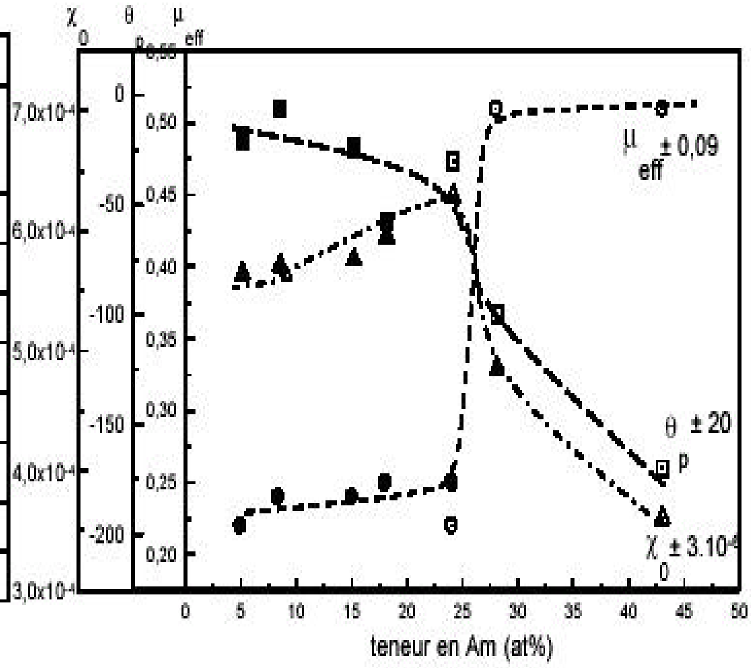
		uem/mole de Pu		
%Am	θp	χ_0 (uem/mole de Pu)	C (K^{-1})	μ_{eff} (μ_B)
4,9	-21	$5{,}64.10^{-4}$	0.006	0,22
8,3	-6	$5{,}71.10^{-4}$	0.007	0,24
15	-24	$5{,}76.10^{-4}$	0.007	0,24
18	-58	$5{,}95.10^{-4}$	0.008	0,25
24	-30	$6{,}29.10^{-4}$	0.008	0,25
24	-30	$6{,}29.10^{-4}$	0.006	0,22
28	-100	$4{,}85.10^{-4}$	0,033	0,51
43	-170	$3{,}61.10^{-4}$	0,033	0,51



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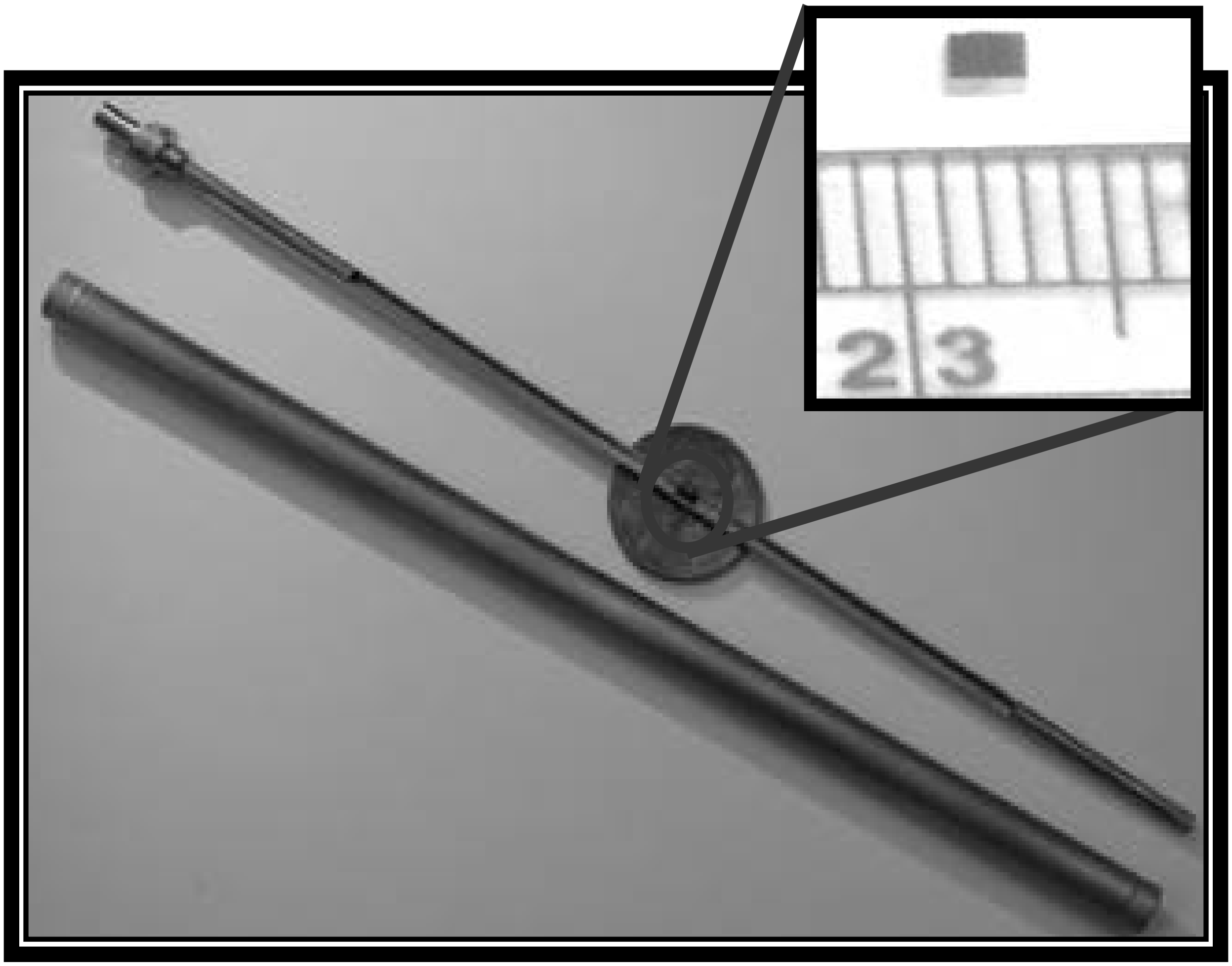

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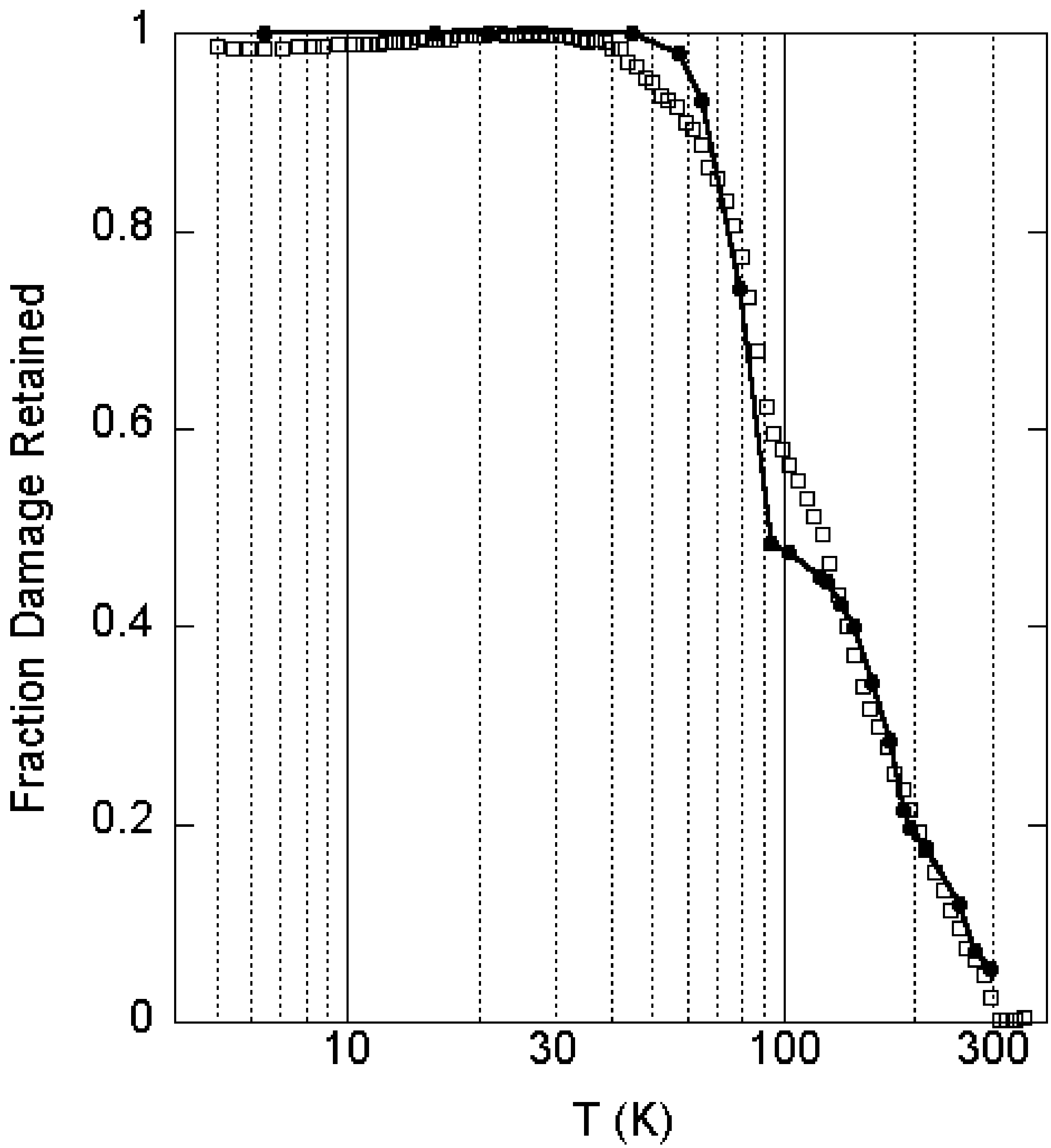

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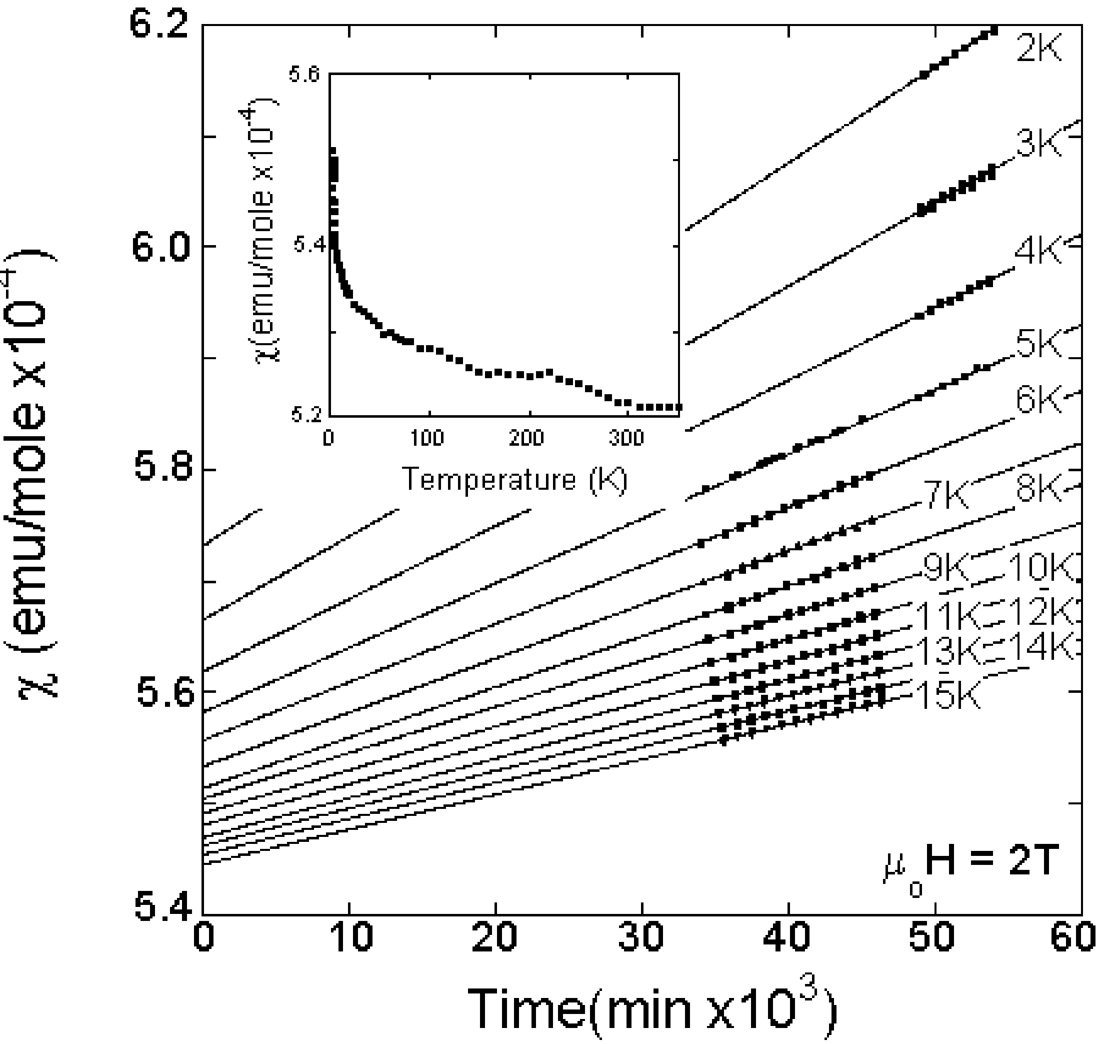

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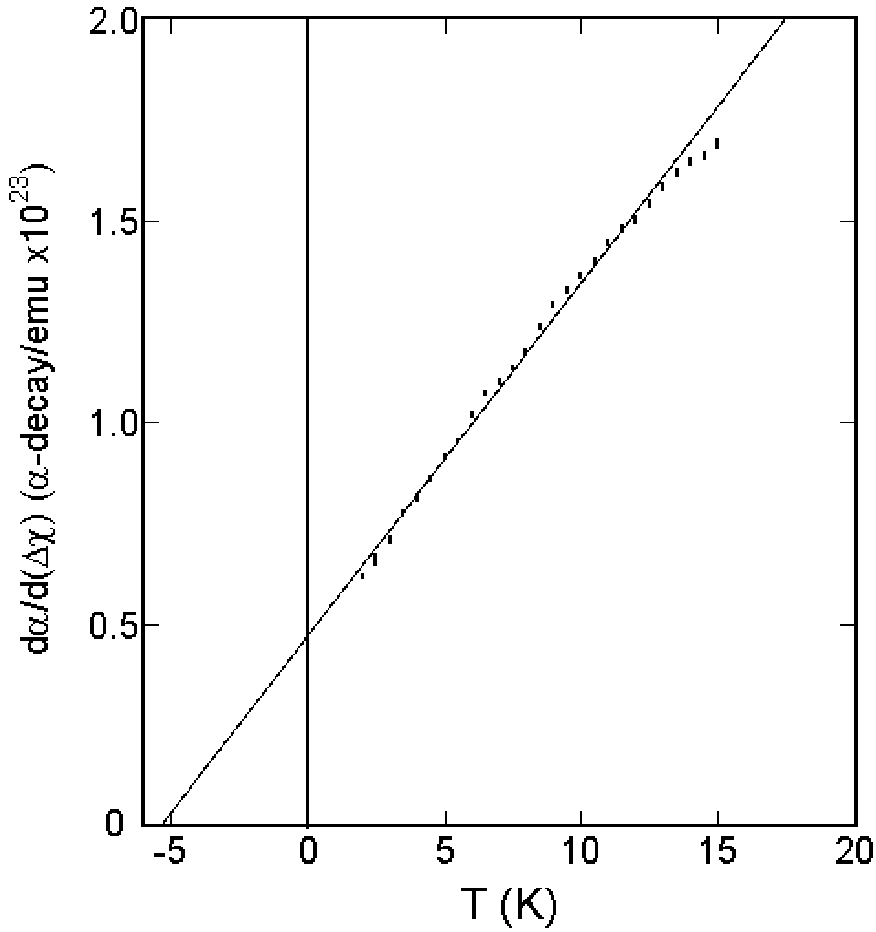

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