Requirements for x-ray magnetic circular dichroism on paramagnetic biological systems and model compounds

Tobias Funk,[a] Stephan Friedrich, Anthony Young, Elke Arenholz, and Stephen P. Cramer

Lawrence Berkeley National Laboratory, Berkeley, California 94720

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We have built an end station for x-ray magnetic circular dichroism (XMCD) measurements on proteins and paramagnetic compounds. Our current setup reaches a base temperature of 2.6 K and magnetic fields up to 6 T and is operated at beamline 4.02 of the Advanced Light Source. In this article we discuss magnetic field and low temperature requirements needed to perform XMCD experiments on magnetically saturated samples. For a typical $3d$ transition metal paramagnetic system we find that fields above 4 T at a temperature of 2.6 K saturate the magnetization of the sample to more than 80%. We discuss principal considerations for a setup operated at low temperatures on a synchrotron and show that infrared heat shielding is unavoidable to obtain the base temperature at the sample. We show first experimental results from the vanadium (IV) compound $VOSO_4X[H_2O]$.   © *2002 American Institute of Physics.*   [DOI: 10.1063/1.1445829]

I. INTRODUCTION

X-ray magnetic circular dichroism (XMCD) is a well-established method to explore the magnetic properties of materials. XMCD is based on the observation that differences in the L-edge absorption spectra with left and right circularly polarized light are related to the magnetization of the sample.[1] The method derives its strength from the fact that sum rules can be applied to derive the orbital $\langle Lz \rangle$ and spin $\langle Sz \rangle$ moment of the sample.[2,3] Most XMCD studies investigate ferro- or antiferromagnetically ordered systems. Hardly any studies are done on paramagnetic systems, which require much higher fields and much lower temperatures. However, applying XMCD to paramagnetic systems like complex chemical compounds and even biological systems gives the possibility to study important chemical properties like spin and oxidation states. This is especially true since XMCD is element selective and thus enables studying a certain atomic species in a complex chemical environment.

Our interest is to study metalloproteins with XMCD. These macromolecules containing 10 000 or more atoms perform catalytic functions in a so-called active site. Typically these active sites are clusters of metal atoms ligated to elements like sulfur, carbon, and nitrogen. Oxidation state and spin state of these metal centers are of high scientific interest.[4] In order to bring the results in a systematic context we study model compounds containing metal atoms. These more concentrated samples can be studied using total electron yield (TEY) while dilute samples are studied using fluorescence yield (FY).[5] In this article we discuss requirements for a XMCD chamber to measure paramagnetic $3d$ transition metal compounds and biological samples. Furthermore we discuss principal considerations necessary to obtain the low temperature at the sample needed for the measurement.

[a] Electronic mail: funk@lbl.gov

II. MAGNETIZATION OF PARAMAGNETIC COMPOUNDS

Studies on paramagnetic systems require magnetically saturated samples. The magnetization M of a paramagnetic system of N noninteracting atoms in a volume V is given by[6]

$$M = \frac{N}{V} \cdot g_J \cdot \mu_B \cdot J \cdot B(x,J),$$

where J is the total angular momentum, g_J the g factor, and μ_B the Bohr magneton. The Brillouin function B is given by

$$B(x,J) = \frac{(2J+1)}{2J} \coth\left(\frac{(2J+1)}{2J} x \right)$$
$$- \frac{1}{2J} \coth\left(\frac{1}{2J} x \right) \quad \text{with} \quad x = \frac{J g_J \mu_B H}{k_B T},$$

where H is the magnetic field and T the temperature. In the pure atomic case one can calculate J using Hund's rules. The situation becomes far more complicated in the presence of crystal fields. The orbital momentum is partly or fully quenched, hence the magnetic moment changed. We apply a crude model to estimate this case. It is reasonable to assume that Hund's rules are still valid, but that the orbital momentum is reduced by say 90% of the undisturbed value. Using the disturbed and undisturbed model we can get a field and temperature range necessary to perform XMCD experiments with a magnetization in or close to saturation.

We discuss here the case of vanadium as an example for a transition metal with a less than half filled d shell. For Ni with a more than half filled d shell we obtain similar results. The different oxidation states result in a d^3 (V^{2+}), a d^2 (V^{3+}), and a d^1 (V^{4+}) configuration of the $3d$ shell. The magnetization for these three cases is shown in Fig. 1 where a base temperature of 2.6 K is assumed and a magnetic field up to 6 T. For all three cases the magnetization is relatively far from saturation. The situation is changed assuming a reduction of the orbital momentum (Fig. 2). For all oxidation
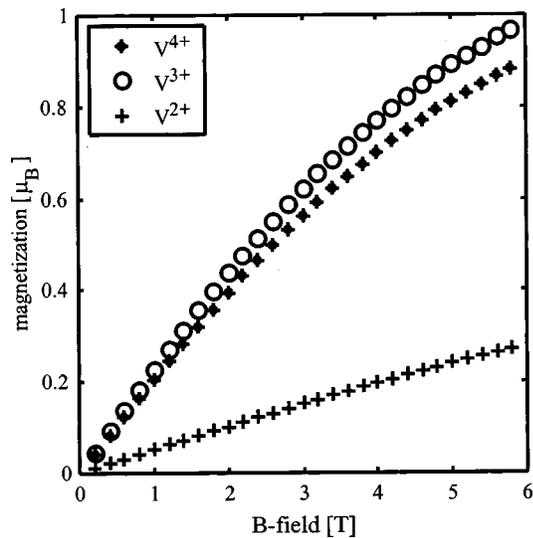
FIG. 1. Magnetization vs B field at 2.6 K for different oxidation states of vanadium. The orbital momentum is fully included.

states the magnetization is more than 80% saturated with fields above 4 T. This is due to the fact that in atoms with a less than half filled shell, orbital (L) and spin (S) angular momentum are antiparallel, hence by reducing L the effective J is enhanced. Consequently temperatures around 2 K and fields above 4 T are needed to perform XMCD experiments with magnetization close to saturation.

III. LOW TEMPERATURE REQUIREMENTS FOR THE EXPERIMENTAL REALIZATION

The XMCD experiment is performed at the elliptically polarizing undulator beamline 4.02 of the Advanced Light Source. The end station accommodates a liquid-helium-cooled cryostat with a superconducting magnet reaching fields up to 6 T and is operated at a base pressure of 6 $\times 10^{-9}$ mbar. The sample stage consists of a pumped liquid He insert to which a sample block is attached. The sample
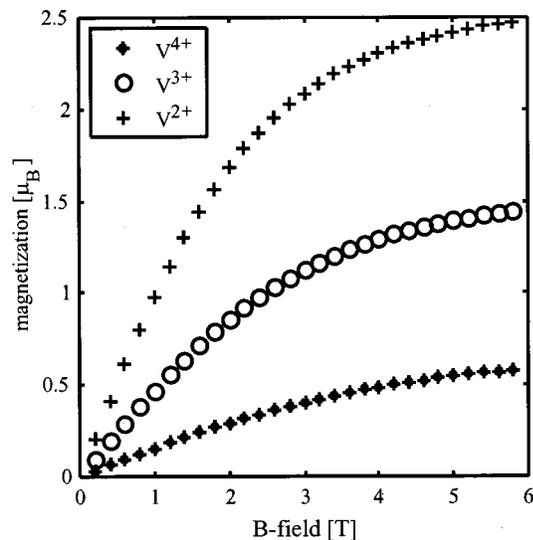
FIG. 2. Magnetization vs B field at 2.6 K for different oxidation states of vanadium assuming a reduction of the orbital momentum to 10% of its atomic value.
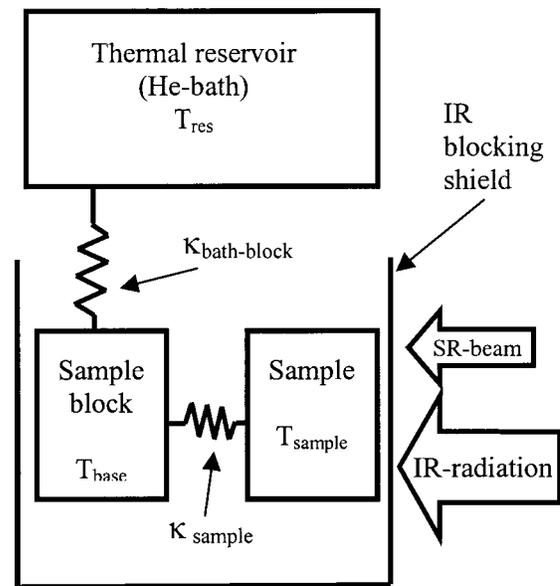
FIG. 3. Block diagram of the experimental setup showing dominant heat loads and thermal resistances.

block is electrically isolated from the He bath by a sapphire disk to allow TEY measurements. Figure 3 shows a block diagram of the sample stage. The sample is mounted to a sapphire or metal disk. This disk is glued with double-sided conducting carbon tape to a sample holder, which is screwed to the sample block. The sample temperature is measured with a CGR thermometer attached to the sample block. An IR radiation shield anchored to the cryostat reduces the IR heat load. To allow the SR beam to reach the sample and the fluorescent light to reach the detector two windows are machined in the heat shield. The windows are covered with IR blocking filters consisting of 100 nm Al on 100 nm parylene. Pumping on the insert we obtain a base temperature (T_{base}) of 2.6 K on the sample block.

Since there is no direct way to measure the temperature at the sample surface (T_{sample}) we have performed calculations to determine the heat transfer. Using the heat flow equation[7]

$$\dot{Q} = \frac{A}{L} \int_{T_{base}}^{T_{sample}} \kappa(T)dT$$

one can calculate T_{sample} for a certain heat load $\dot{Q}$ and thermal conductivity $\kappa(T)$. A is the area of the beam spot and L the thickness of the sample. The thermal conductivity in our setup is determined by the thermal resistance of the sample and by the boundary (Kapitza) resistance. We assume that the thermal conductivity of a protein or an insulating compound is in the range of typical insulators [10^{-3} W/cm K $< \kappa$(4 K) $< 10^{-5}$ W/cm K], that the Kapitza resistance is 6 $\times 10^{-4}$ W/K, and both have a T^3 dependence.[7,8] The beam spot A is approximately 150 by 600 μm^2. The film thickness is of order the attenuation length of the Al K-fluorescence (≈ 7 μm) since we detect second order excitations of the sapphire substrate.

The heat load $\dot{Q}$ into the sample is given by the IR radiation from surfaces at higher temperatures and by the SR
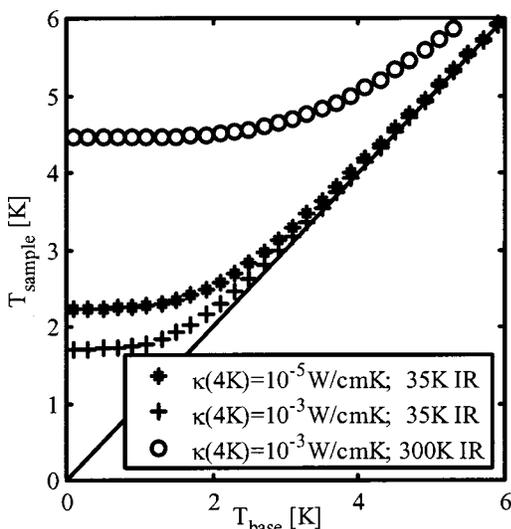
FIG. 4. Sample temperature vs base temperature. The solid line shows the ideal case of infinitely good thermal conductivity.

FIG. 5. XMCD spectrum of the vanadium (IV) compound $VOSO_4X[H_2O]$.

beam with a flux of 10^{12} photons/s. With a photon energy of 500 eV we calculate the deposited power to 80 μW. For the IR heating we first calculate the case without IR blocking windows present hence the sample is exposed to room temperature IR radiation. In the second case we calculate the heat load to the sample using IR blocking windows. Although the blocking windows are anchored to the heat shield, their average temperature is much higher than the heat shield temperature. We have performed a simulation for our setup using the model and parameters described in Friedrich *et al.*[9] The maximum temperature on the windows we compute to 35 K. We use this temperature to calculate the IR heat load assuming an emissivity of 1 for the sample. The results of our simulation are shown in Fig. 4 using the nomenclature as defined in Fig. 3. T_{sample} is plotted as function of T_{base}, the solid line shows the ideal case of infinite thermal conductivity where $T_{sample} = T_{base}$. Exposing the sample to 300 K IR radiation leads to a significant deviation between T_{sample} and T_{base}. In this case the lowest possible sample temperature is 4.4 K. For both cases where we assume a 35 K IR radiation the simulation starts to depart from the solid line around 2.5 K. We conclude that for our experimental situation the sample temperature is equal to the measured base temperature.

IV. RESULTS

Figure 5 shows a XMCD spectrum of the vanadium (IV) compound $VOSO_4X[H_2O]$ taken in the TEY mode. The sample temperature was 2.6 K, the B field -5.1 T, and the degree of circular polarization was 90%. The noise of the spectrum results from the insulating properties of the sample. The spectrum shows a clear difference between left and right circularly polarized light and demonstrates that XMCD spectroscopy on paramagnetic V systems is feasible.
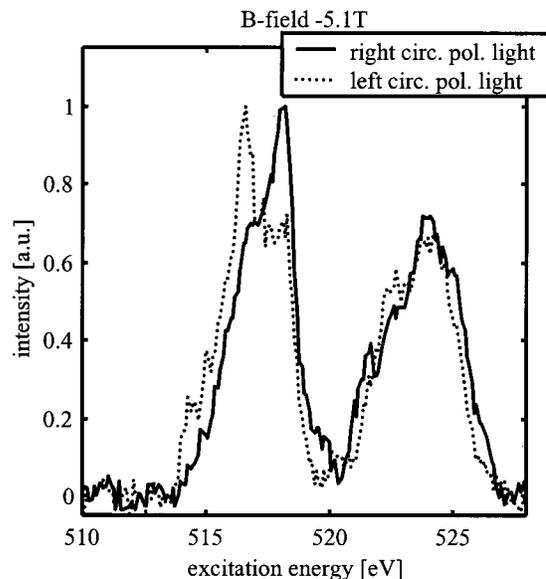
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