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用热解石墨晶体作色散和聚焦光学元件的激光等离子体源的超快 X 射线光谱仪

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摘要:由于激光等离子 X 射线源的光子通量显著低于同步辐射源的光子通量且射线为所有方向的各向同性辐射,所以,很需要具有大的集光立体角和高的积分反射率的光学元件,用热解石墨(PG)晶体作色散和聚焦元件可满足上述要求。由于 PG 晶体为嵌镶结构,所以可给出很高的积分反射率,而 PG 薄膜还可安装在任意形状的模具上构成任意形状的光学元件。此外,特殊形状的嵌镶聚焦使这些晶体甚至在弯曲的情况下,也可作为高分辨率 X 射线光学元件。基于上述元件特性,可以设计出有高集光效率的色散光学元件,用于激光等离子体源超快 X 射线光谱检测。文中描述了 PG 弯晶在一台改型的 von HAMOS 光谱仪中的应用,使用这台光谱仪,测量了飞秒激光器产生等离子体发射的 X 射线的光谱分布。讨论了产生的 X 射线在时间分辨扩展 X 射线吸收精细结构(EXAFS)分析中的应用。实验表明,通过优化晶体特性和光谱仪几何设置,可以实现对过渡金属 K 边的高分辨率 EXAFS 测量。

关　键　词:X 射线光谱仪;激光等离子体 X 射线源;热解石墨晶体;色散;聚焦
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Pyrolytic graphite crystals as components for ultrafast X-ray spectroscopy using laser-based sources

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Abstract: Because the photon flux of laser-based X-ray sources is considerably lower than that of synchrotron radiation sources and radiation is emitted isotropic in all directions, focusing optics with a large solid collecting angle and high integral reflectivity are required. For these requirements crystals of Pyrolytic Graphite (PG) are of particular interest for the use as dispersive and focusing elements. Due to the mosaic crystal structure, PG exhibits a very high integral reflectivity. Furthermore, thin PG films give the opportunity to realize crystal optics with arbitrary geometry by mounting them on a mold of any shape. Beyond that, mosaic focusing in specific geometry allows these crystals to be used as high resolution X-ray optics, even in bent geometry. All these properties allow the design of highly efficient dispersive collecting optics for ultrafast X-ray spectroscopy with laser plasma sources.

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In our contribution we describe the application of bent PG crystals in a spectrometer with a modified Von HAMOS geometry. Using this spectrometer, the spectral distribution of the X-ray radiation emitted from a fs laser produced plasma has been measured. The application of this radiation for time-resolved Extended X-ray Absorption Fine Structure (EXAFS) experiments is discussed. We show that, by optimizing both the crystal properties and the spectrometer geometry, a good spectral resolution sufficient for EXAFS measurements at the K-edges of transition metals can be achieved.

Key words: X-ray spectroscopy; laser-based source; pyrolytic graphite crystal; dispersion; focusing

1 Introduction

Extended X-ray absorption fine structure spectroscopy (EXAFS) in chemical, biological and material science with the aim of investigating molecular structures is today mostly performed with synchrotron radiation[1]. Laboratory X-ray spectrometers can be operated with table-top X-ray sources as *e. g.* X-ray tubes or for time-resolved studies with laser plasma-produced sources (LPP)[2-5]. Because the photon flux of these sources is considerably lower than that of synchrotron radiation sources, focusing optics with a large solid collecting angle is required[6]. Time-resolved investigation of X-ray emission from laser-produced plasma as well as application of these sources in ultrafast X-ray pump-probe spectroscopy requires a spectrometer design that combines highest-possible spectrometer efficiency (high integral reflectivity) and high spectral resolution. Crystals of Highly Oriented Pyrolytic Graphite (HOPG) are of particular interest for the use as dispersive elements because their unique structure enables them to be highly efficient in X-ray diffraction[7]. HOPG is a mosaic crystal formed by a large number of small crystallites. The angular distribution of these crystallites, with plane orientations of the normal axis to the surface, is called mosaic spread. Mosaicity makes it possible that even for a fixed angle of incidence to the crystal surface, an energetic distribution of photons can be reflected because each photon of this energetic distribution can find a crystallite plane at the right Bragg angle. The width of this energetic distribution depends on the mosaic spread. The mosaicity is responsible for the dramatic increase of integral reflectivity for mosaic crystals in comparison to perfect crystals. The mosaicity also gives rise to so-called parafocusing[8], which enhances the intensity in the image plane. Furthermore thin HOPG films give the opportunity to realize crystal optics with arbitrary geometry by mounting on a mold of any shape. This enables the design of crystal optics with high collecting efficiencies. In our contribution we describe the spectral properties of HOPG crystals in a modified Von HAMOS geometry[9] with respect to an application in ultrafast X-ray spectroscopy.

2 Experiments

The experimental arrangement consisted of HOPG crystals (with thicknesses ranging from 10 ... 150 μm, provided by Optigraph GmbH, Berlin) mounted on flat surfaces, an X-ray tube and a CCD camera. All measurements were performed in a modified Von HAMOS geometry with the detector plane oriented perpendicular to the reflected X-ray beam (Fig. 1).

The X-ray source, which was used for the characterization of the HOPG optics, was a low-power microfocus X-ray tube (IfG GmbH Berlin,[10]) with a source diameter of 50 μm. The source was operated with different anode materials (Cu and Ag) at a voltage of 40 kV and an anode current up to 400 μA for the Cu anode and up to 700 μA for the Ag anode. For detection of the hard X-ray emission, a 16 bit deep

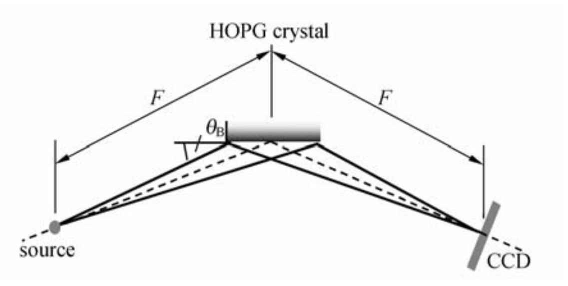


Fig. 1 Experimental setup for the characterization of HOPG crystals

depletion CCD-camera (PI-LCX 1300 Roper Scientific) with a quantum efficiency of about 0.5 at 8 keV was used. The camera was sealed with a thin (250 μm) Be window, so that a deep cooling (down to −50°) of the CCD was possible. Scattered X-ray radiation was suppressed by screening the camera with Pb plates. The investigations were performed for different distances, whereby the distances between the source and the crystal and the crystal and the detector were equal in each measurement. In this configuration, parafocusing (= mosaic-focusing) takes place and the highest energy resolution becomes possible.

To prove the application of the crystals time-resolved X-ray spectroscopy experiments with a laser produced plasma source were performed. The radiation from a Ti:sapphire laser (35 fs pulse duration, 10 Hz repetition rate, single-pulse energy on target up to 400 mJ) was focused in a vacuum chamber by an Off-axis Parabolic (OAP) mirror on a tape target system. As target material, both copper and tungsten tapes with thickness of 50 μm were used. The hard X-ray radiation emitted in 2π from the laser-produced plasma was filtered by a thin Be foil (250 μm), which sealed the vacuum chamber. In order to protect the window and the focusing optics against the debris produced by the plasma source, a foil was placed between the source and these components. The HOPG crystal and the deep depletion CCD camera were placed outside the vacuum chamber. The distance between the source and the crystal, as well as between crystal and CCD camera was 340 mm.

3 Results

3.1 Spectral resolution of HOPG crystals

The spectral resolution of thin films of HOPG has been investigated in (002)-reflection and (004)-reflection orders[11]. In order to optimize the spectral resolution, the distances *F* (Fig. 1) between the source, the crystal and the detector have been varied over a wide range. As an example, the results of the measurements for 150 μm and 15 μm thick crystals are summarized in Fig. 2. As can be seen from Fig. 2, the Cu $K\alpha_1$ and $K\alpha_2$ lines, which are separated by 20 eV, are clearly resolved for all distances. The energy resolution of HOPG films (Fig. 3) for different distances and thicknesses was obtained from the recorded spectra by a convolution procedure. For the convolution a natural line width of 2.3 and 3.5 eV[12] for the Cu $K\alpha_1$ and $K\alpha_2$ lines was assumed (see also [11, 13]). As expected, the spectral resolution obtained for the (004)-reflection is clearly better than that of the (002)-reflection, because of the larger Bragg angle in (004)-reflection. The best value of $E/\Delta E = 2\,900$ was obtained for the largest distance of $F = 260$ mm and smallest thickness of $d = 15$ μm. As can be seen from Fig. 3, the energy resolution depends on both the crystal thickness and the geometry of the spectrometer setup. This behaviour can be explained by the mosaicity of the crystal. In contrast to ideal crystals, the photon in mosaic crystals has to penetrate to some depth, before it finds a crystallite aligned well from which it can be reflected. That means that the effective depth, from which diffraction in mosaic crystals occurs, is much larger compared to ideal crystals. This diffraction out of the depth reduces the energy resolution and can only be overcome by using thinner HOPG films or by enhancing the distances between the crystal and detector. Both are possible, because the thickness of the HOPG crystals can be easily adjusted. On the other hand, reducing the crystal thickness results in a reduction of the integral reflectivity, because fewer crystallites can participate in the diffraction process. On the other hand enhancing the distance *F* reduces the collecting angle for a given crystal optic. This issue can be overcome using bent crystals with a large collection angle. For the 150 μm crystal, the integral reflectivity amounts to 0.9 mrad for (004)-reflection and 4.6 mrad for (002)-reflection. In comparison, the 15 μm HOPG crystal exhibits a integral reflectivity, which was about a factor of 10 lower than the related value for the 150 μm thick crystal[13].

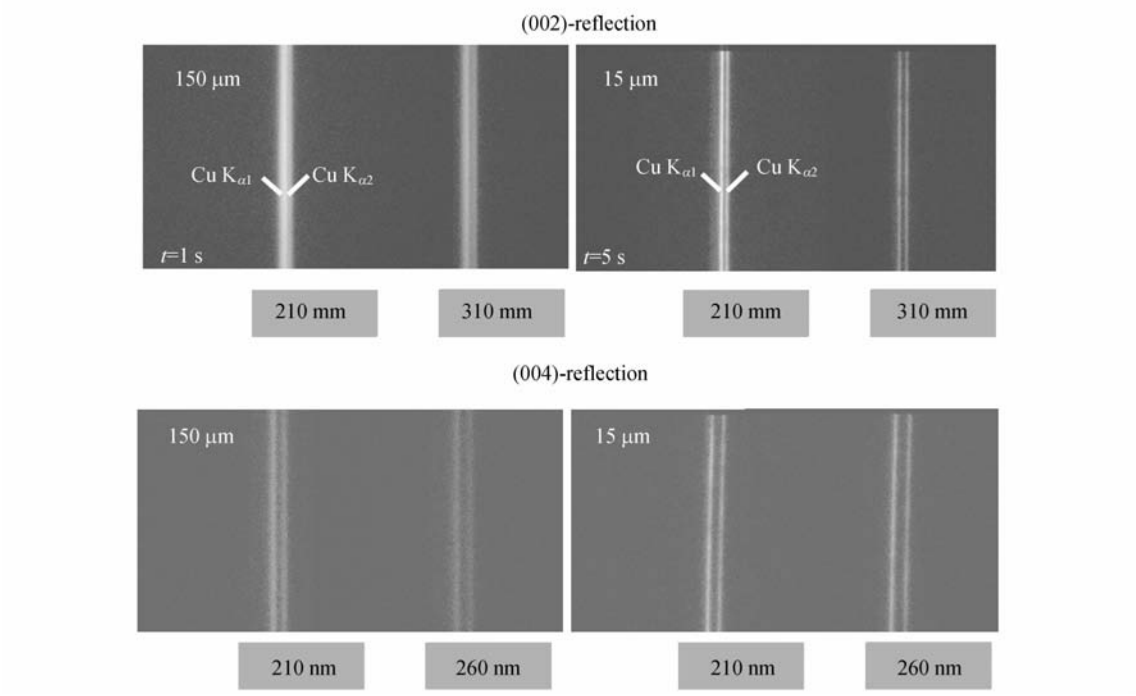
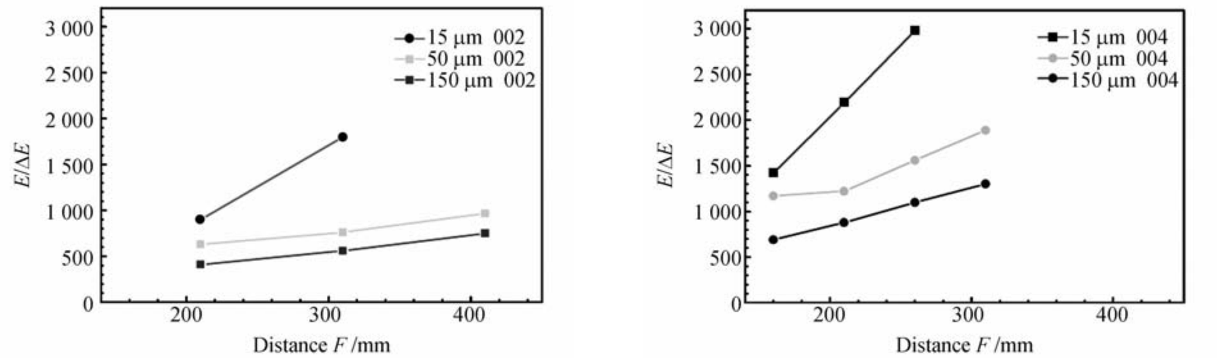


Fig. 2　Measured CCD images of the recorded Cu Kα lines at different distances *F* between source-crystal and crystal-detector (1∶1 geometry) for flat HOPG crystals



(a)　　(b)

Fig. 3　Energy resolution for different HOPG crystal in dependence on the distance *F* between source-crystal and crystal-detector for (002)-reflection (a) and (004)-reflection (b). The energy resolution was estimated from a convolution procedure using the natural width of Cu Kα lines and a spectrometer function given by Voigt profile

Consequently the energy resolution and the integral reflectivity must be optimized for a chosen spectrometer geometry. It should be pointed out, that an upper limit for the energy resolution is given by the intrinsic width of the Bragg reflection for HOPG (see also Ice and Sparks[14]). Unfortunately, this energy resolution cannot be achieved in practice, because of an extended source, aberrations of the spectrometer geometry and other focusing errors causing further broadening. The effect of such geometrical factors can be taken into account using ray-tracing calculations[15]. A comprehensive description of the contribution of the different factors, which limits the spectral resolution, can be found in a forthcoming paper[16].

3.2 X-ray spectroscopy with HOPG crystals

With an energy resolution $E/\Delta E$ better than 1 000 at the transition metal K-edges, nearly all features of the EXAFS spectra can be resolved. In order to prove the potential of the HOPG spectrometer for X-ray absorption experiments the filtered Bremsstrahlung continuum emitted by the microfocus X-ray tube (operated with an Ag-anode) behind a 4 μm Ni foil (Goodfellow) was collected in the (004)-reflection. The Ni foil was placed between source and the 150 μm thick crystal mounted on a plane glass plate. The distance F was 340 mm and corresponds to a measured spectral resolution of $E/\Delta E=1\ 200$ (cp. Fig. 3). Slits were placed behind the source and in front of the CCD camera to reduce the scattering background. The CCD image of the filtered Bremsstrahlung continuum and the EXAFS spectrum of the metallic Ni foil, resulting from a measurement with and without the foil, are shown in Fig. 4. The integration time for recording this spectrum was 600 s. As can be seen from Fig. 4, the Ni K-edge and all EXAFS oscillation are clearly resolved. This result demonstrates the applicability of HOPG crystals for EXAFS spectroscopy. Recently it has been shown that bending of thin PG films does not influence the energy resolution[16]. That means that optimizing the spectrometer setup, *e. g.* by using bent crystals in a focusing geometry, will further enhance the energy resolution and reduce the acquisition times.

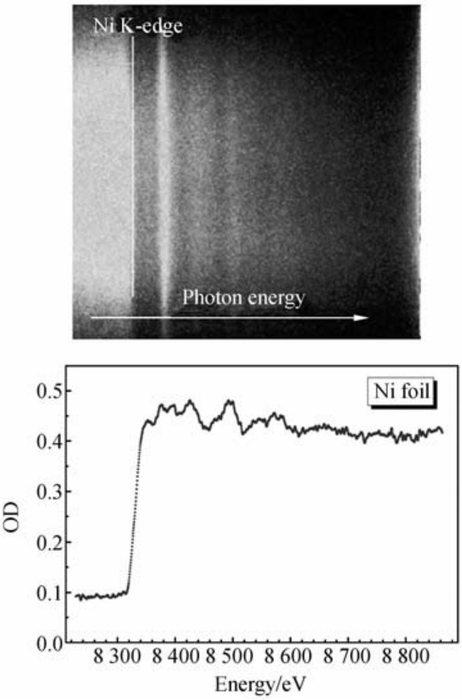


Fig. 4 Image of the Ni K-edge absorption measured with a 150 μm HOPG crystal in (004)-reflection order using a mircrofocus tube at $F=400$ mm (up). Extended absorption fine structure of a 4 μm Ni foil derived from the image (down). The data acquisition time was 20 min

3.3 Ultrashort laser plasma source for X-ray spectroscopy with HOPG crystals

With regard to an application of the HOPG spectrometer for X-ray pump-probe spectroscopy with ultrashort pulses emitting laser plasma sources, emission spectra of a tungsten plasma were measured with the 150 μm thick HOPG crystal. An image of the measured spectrum in the (004)-reflection is shown in Fig. 5 together with the tungsten emission spectrum around the Ni K-edge. The acquisition time for this spectrum was 30 s.

The energy resolution, which results from these spectra is comparable to those obtained with the X-ray microfocus tube. That means that the laser plasma source size does not affect the spectral resolution of the spectrometer setup.

As can be seen from Fig. 5 the X-ray plasma

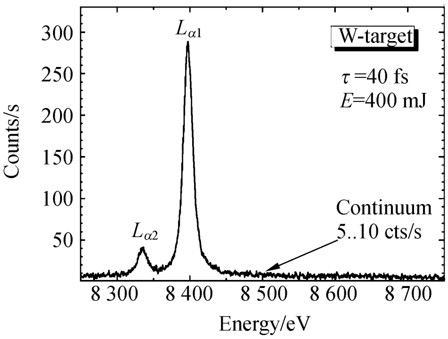


Fig. 5　Emission from a laser produced tungsten plasma recorded with a 150 μm HOPG crystal at $F=360$ mm. Besides the characteristic $L_{\alpha1}$ and $L_{\alpha2}$ bands a continuum background is clearly visible. Laser parameter: Ti. Sa laser with 400 mJ single pulse energy, pulse duration: 40 fs, repetition rate 10 Hz, data acquisition time 30 s

emission spectrum consists of continuum radiation (Bremsstrahlung) suitable for X-ray absorption spectroscopy and the characteristic W Lα radiation. The radiation originates from hot electrons generated by non-linear laser light absorption in the plasma. This radiation can be expected to have pulse length in the order of some hundred femtoseconds[4,18-20]. The X-ray emission spectrum of the W laser plasma source shows a Bremsstrahlung continuum, whose intensity magnitude is about two orders lower than the W *L*α line emission. This Bremstrahlung continuum is sufficient to perform EXFAS measurements at the Ni or Co K-edge, as already shown[3]. In comparison to the spectrometer with Si(111) crystals, which were used so far for X-ray spectroscopy based on laser produced plasma sources, the recording times can be reduced significantly with the HOPG spectrometer. In this way, instabilities of the experiment can be overcome, such as the emission instability of laser plasma sources over a long period and a degradation of the sample over many hours.

4 Conclusions

Crystals of highly oriented pyrolytic graphite are a promising candidate as dispersive element for X-ray "pump-probe" spectroscopy using ultrashort laser plasma sources. Besides highest integral reflectivity these crystals can provide energy resolutions of $E/\Delta E>1000$. As demonstrated, such energy resolutions are sufficient to perform EXAFS spectroscopy at transition metal K-edges. The results of first experiments with a HOPG spectrometer and an ultrashort tungsten laser plasma source indicate that the acquisition time, which is necessary to collect an EXAFS spectrum with comparable energy resolution, can be significantly reduced in comparison to spectrometers based on perfect crystals used so far for ultrashort laser plasma spectroscopy[3]. The performance of the measurement can be further enhanced, by optimizing the HOPG spectrometer setup, which was used in the present work. Because thin films of HOPG can be mounted on a mold of any shape, the collecting efficiency and the focusing properties of the spectrometer optics can be improved. Recently we have shown that with PG crystals high energy resolutions are feasible even in bent geometry[17]. Furthermore, the energy resolution of the PG crystals can be improved by an advanced production technology[16]. Using these advanced bent crystals and optimizing the size and the shape of the substrate for the films the acquisition time can be further decreased keeping the energy resolution constant.

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