

A HIGH RESOLUTION X-RAY FLUORESCENCE SPECTROMETER FOR NEAR EDGE ABSORPTION STUDIES

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ABSTRACT

A high resolution fluorescence spectrometer using a Johann geometry in a backscattering arrangement was developed. The spectrometer, with a resolution of 0.33 eV at 6.55 keV, combined with an incident beam, with a resolution of 0.77 eV, form the basis of a high resolution instrument for measuring x-ray absorption spectra. The advantages of the instrument are illustrated with the near edge absorption spectrum of dysprosium nitrate.

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INTRODUCTION

X-ray fluorescence and absorption spectroscopies give important information on structural and electronic properties in the study of materials. Emission spectroscopy is widely employed in the study of the transitions between valence band or near valence band orbitals and inner core hole states. These transitions are sensitive to bonding, oxidation and atomic coordination of the system. The measurement of absorption spectra using fluorescence detection is very powerful for the extraction of weak spectra from dilute samples. The purpose of this communication is to describe a spectrometer which provides the ability to select a small energy window from the fluorescence spectra, which gives new capabilities. In particular, the observation of new spectroscopic features in the near edge region which are normally obscured by the core hole lifetime¹ is made possible. Further, the signal from low energy satellites of transitions such as the $K_{\beta 2}$ of the $K_{\alpha 1,2}$ fluorescence observed for 3d transition metals can provide a means of making spin-dependent^{2,3} and/or oxidation-specific absorption measurements.

THE SPECTROMETER

X-ray emission spectra are routinely analyzed with crystal spectrometers. These instruments fall into two general classes: Rowland circle instruments and double crystal instruments. Synchrotron based experiments by the NIST Group^{3,4} on gases have shown the power of Rowland circle instruments. Double crystal instruments have been used for example in the study of emission spectra from Mn^{4+} . Both Rowland circle and double crystal instruments can provide good resolution. The double crystal instrument, in the (+,+) arrangement, however, has small angular acceptance, limited by the Darwin width of the Bragg reflection. The conventional Rowland circle geometries with low order Bragg reflections suff-

fer either from source size contributions to resolution and/or throughput. This is easily understood by taking the logarithmic derivative of Bragg's law⁵³

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta\tau}{\tau} + \cot(\theta)\Delta\theta \quad (1)$$

The $\frac{\Delta\tau}{\tau}$ term, in the absence of strain, is just the contribution of the Darwin width and the $\cot(\theta)\Delta\theta$ term is the contribution from the source size and the spatial resolution of the detector. It is immediately apparent from Eq. (1) that for Bragg angles near 90° the contribution of the source size to resolution can be drastically reduced. Indeed, backscattering techniques have been used for very high resolution inelastic scattering studies of both neutrons⁵⁴ and x-rays⁵⁵. There is an additional advantage to backscattering. As mentioned above 'conventional' Rowland circle instruments work with low order Bragg reflections. In order to increase solid angle for these instruments a crystal shape which is a surface of revolution about the line joining source and detector is required. In general this is a complicated aspheric. In backscattering, however, a simple sphere is an excellent approximation to the needed aspheric thus providing at once both good resolution and large solid angle.

Based on this argument, a spectrometer was constructed that permitted the measurement of a narrow band of an emissions spectrum. In turn absorption spectra were recorded by monitoring the intensity in this narrow band as the incident energy was varied. The spectrometer was built around a large 4-circle Huber goniometer at the X25 hybrid wiggler beam line at the National Synchrotron Light Source, at the Brookhaven National Laboratory⁷⁷. The optics of this beam line consists of a Pt coated double focusing mirror collecting about 1.5 mrad of the horizontal opening angle and a two crystal Si(220) monochromator. The focus of this beam line is 283 mm away from the source with a beam size about 0.5^2 mm². The measured resolution for the monochromator is 0.7 eV at 6.5 keV and the

monochromatic flux is of the order of 10^{11} photons/s, when 0.5 horizontal mrad are used.

The spectrometer operated in the vertical plane. The sample was placed at the center of the goniometer located at the focus of the beam. The spectrometer, consisting of an analyzer crystal and detector, with the sample as the source, uses the Johansson geometry⁹³ on a 900 mm diameter Rowland circle (Fig. 1a). The analyzer was a spherical Si (440) crystal. Its figure was achieved by elastically bending a parallel-faced silicon crystal wafer, 75 mm in diameter and 1 mm thick, to a radius of 900 mm. The analyzer subtends a solid angle of 0.6 msr. Optical and x-ray measurements showed that the coaxial fixture⁹³ shown schematically in Fig. 1b, and used to bend the crystal, produced a spherical shaped curvature. Measured figure errors were about $175 \mu\text{rad}$. This corresponds to twice the Darwin width at $\theta_{\text{BB}} = 83.38^\circ$ and accounts in part for the observed 0.3 eV resolution at 65 keV. This level of performance however is sufficient for the present application.

The detector is a linear position sensitive gas proportional counter (PSD). Over the full length of 100 mm it has a spatial resolution of $200 \mu\text{m}^{10}$. In order to reduce the air path, which causes very significant absorption a vacuum chamber was put in between the analyzer and the detector. This arrangement limited the measurements to an angular interval of $\theta = 83.33 - 86.5^\circ$ which corresponds to energies from 6501 eV to 6499 eV. Although in principle a PSD is not needed for the present application it provides ease of alignment and operation of the spectrometer.

The instrument described above with its limited energy range is a prototype. An instrument with more general application can be easily constructed by: (1) making a vacuum path that covers the Bragg angle range from 60° to 90° and (2) utilizing the reflections along the high symmetry directions in Ge and InSb as well as Si. The energy ranges covered by these low index reflections are shown in

Fig. 2. The lower energy limits correspond to the ideal backscattering condition while the upper values correspond to the 60° Bragg angle. This figure also relates the K and L emission lines for different transition metals and rare earths and the proper low index crystal reflection.

RESULTS AND DISCUSSION

Transition metals are of particular interest because of their magnetic properties. Similar arguments can be used for rare earths. These metals, which extend from lanthanum to hafnium, are characterized by partially filled f shells and are considered to have a complicated valence band structure. To demonstrate the applications of this spectrometer to near edge absorption studies, the rare earth, Dy, was chosen.

Fig. 3 shows the measured L_{α_1} fluorescence line from a dysprosium nitrate compound. The incident energy was 500 eV above the Dy L_{III} absorption edge. The asymmetry of the line is due to the vacuum chamber wall which limits the range of the analyzer Bragg angle, as discussed above. The dashed line in the figure represents the analyzer resolution which in this case is more than one order of magnitude better than the natural lifetime width.

In conventional XANES or EXAFES the absorption is studied by measuring the incident beam attenuation in the sample or by monitoring the fluorescence or electron yield while scanning the incident energy through the absorption edge. In the x-ray region the total resolution, determined by the convolution of the incident beam resolution and the natural lifetime width of the core hole, in these experiments is typically of the order of a few eV. However, the core hole lifetime broadening can be overcome if a narrow energy band of the fluorescence radiation is monitored selectively with a high resolution analyzer¹¹. This is simply due to the energy conservation in the fluorescence process which states that the uncertainty

of the photoelectron energy is determined by the uncertainty of the energy of the incident photon, fluorescence photon and final state hole.

The effect of the enhanced resolution obtained with the analyzer described here is demonstrated in Fig. 4. In this figure two identical energy scans from a dysprosium nitrate sample using the conventional transmission technique and the high resolution fluorescence technique are compared. In the transmission case the absorption was measured by monitoring the transmitted beam with an ionization chamber, while for the high resolution case only the narrow bandwidth of the fluorescence spectrum indicated by the dashed lines in Fig. 3 was monitored. The high resolution XANES shows dramatically improved resolution. The extended tail to the low energy side of the absorption edge in the conventional absorption spectrum, resulting from the lifetime broadening contribution to the energy resolution, disappears. A structure which is almost totally invisible in the conventional transmission spectrum is revealed. The absorption edge is seen to be split into two parts: one corresponding to the quadrupole transition to the partially filled 4f states and the second edge and white line corresponding to the dipole transition to the empty 5d states.

SUMMARY

The advantages of the backscattering geometry have been shown to be important for a new technique in the study of absorption spectroscopy. Using the prototype instrument described here new features in the near edge structure at the L_{III} edge of Dy have been observed. Other studies have utilized this instrument to make final state selective absorption studies²¹. The instrument is easily extended to cover the K_{α} and K_{β} fluorescence lines of most of the 3d transition metals, and the L_{α} and L_{β} fluorescence of the 4d metals and the rare earths.

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References

¹K. Hamalainen, D. P. Siddons, J. B. Hastings and L. E. Berman, submitted for publication.

²K. Hamalainen, C.-C. Kao, J. B. Hastings, D. P. Siddons, L. E. Berman, V. Stojanoff and S. P. Cramer, submitted for publication.

³See for example: P. L. Cowan, *Physica Scripta* **T31**, 1122 (1990) and references therein; B. D. Deslattes this Proceedings.

⁴Kenjiro Tsutsumi, Hiroo Nakamura and Kouichi Ichikawa, *Phys. Rev.* **B13**, 929 (1976).

⁵M. Hirt, A. Heidman and B. Alefeld, *Nucl. Instr. and Meth.* **95**, 435 (1971).

⁶See for example E. Hurler this proceeding and the references therein.

⁷Tommy E. Berman, J. B. Hastings, Tom Overhizer and Martin Woudle, this Proceedings.

⁸H. H. Johann, *Z. Physik* **69**, 185 (1931).

⁹S. Hagstrom and K. Schiegladin, *J. Ultrastructure Research* **3**, 401 (1960).

¹⁰C. C. Smith, *Nucl. Instr. and Meth.* **222**, 230 (1984).

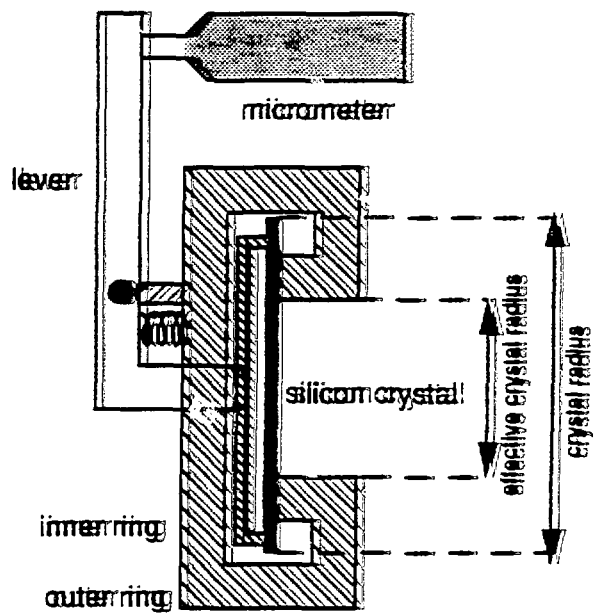
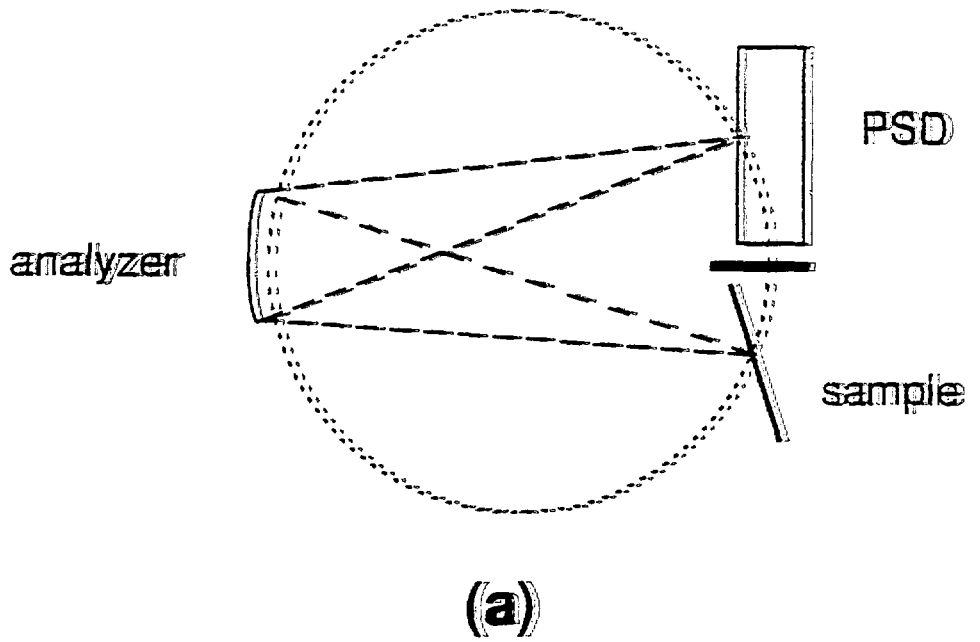
Figure Captions

Fig. 1. Schematics of the experimental setup (a) and spherical crystal bender (b).

Fig. 2. Plot of the K_{α} and K_{β} (a), L_{α} and L_{β} (b), and L_{α} and L_{β} (c), energies for some transition metals and rare earths. On the right panel, the energies covered by low index: (100), (110), (111), and (111) reflections from Si, Ge and InSb are indicated. The lower energy values correspond to a perfect backscattering geometry while the higher value to geometries 30° away from this condition.

Fig. 3. High resolution Dy L_{α_1} fluorescence spectrum obtained by scanning the analyzer. The incident energy for this measurement was 50 eV above the L_{III} absorption edge. The dashed line corresponds to the analyzer resolution, 0.3 eV.

Fig. 4. Conventional and high resolution fluorescence Xanes of Dy. L_{III} . Both measurements were made on the same sample with the same incident photon energy resolution.

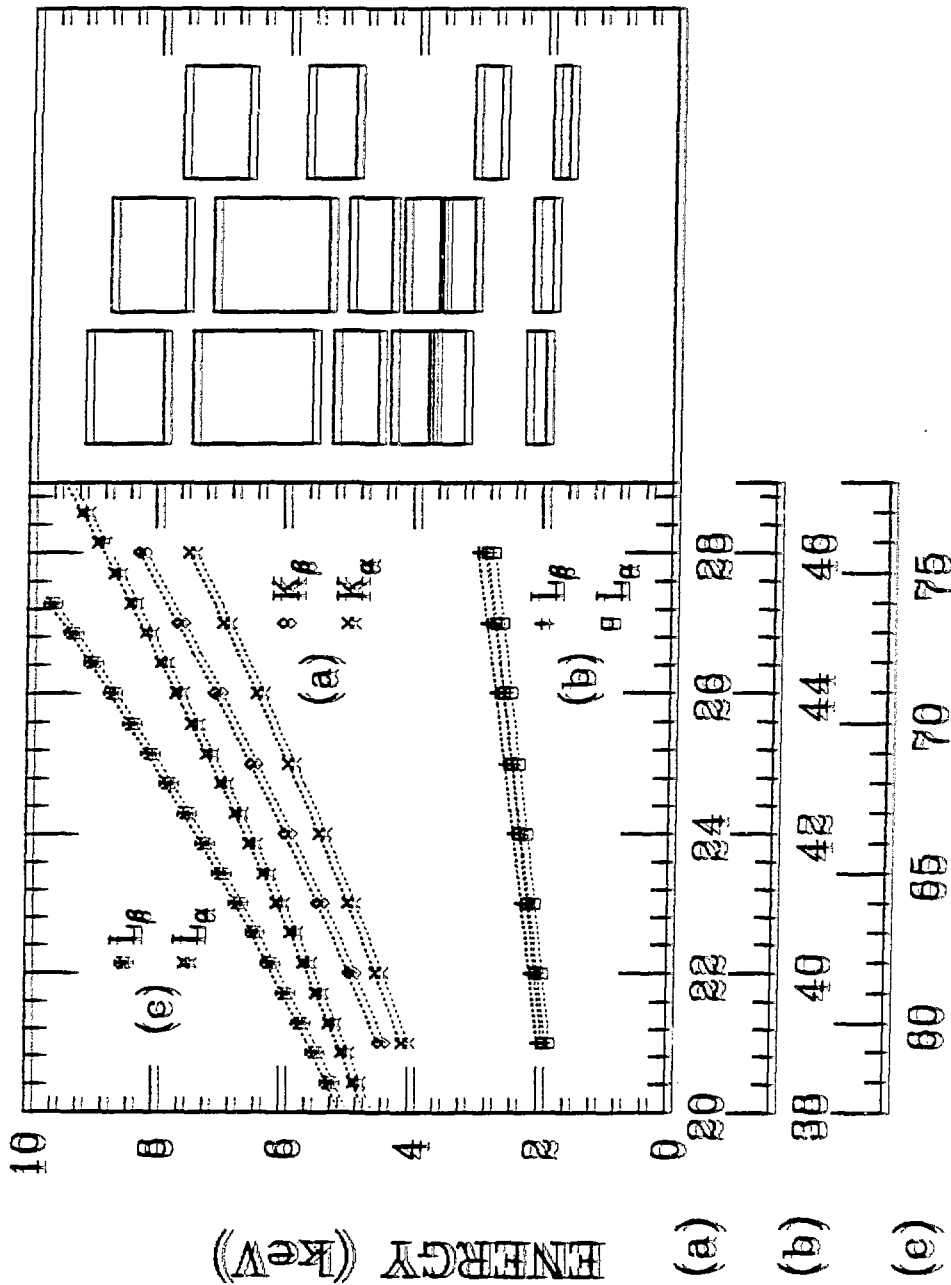


SPHERICAL CRYSTAL BENDER

(b)

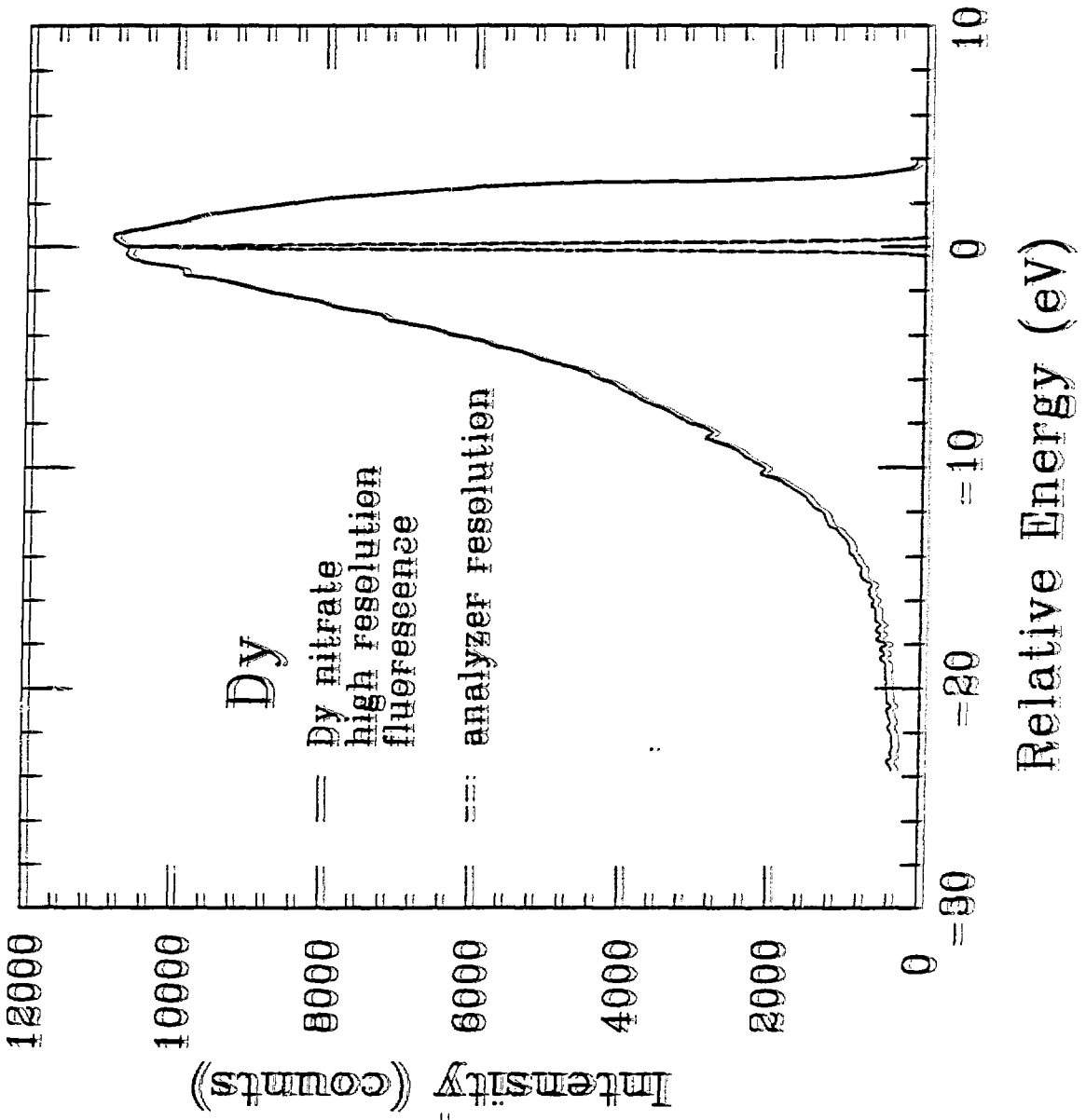
FIG 11

Si Ge In Sb



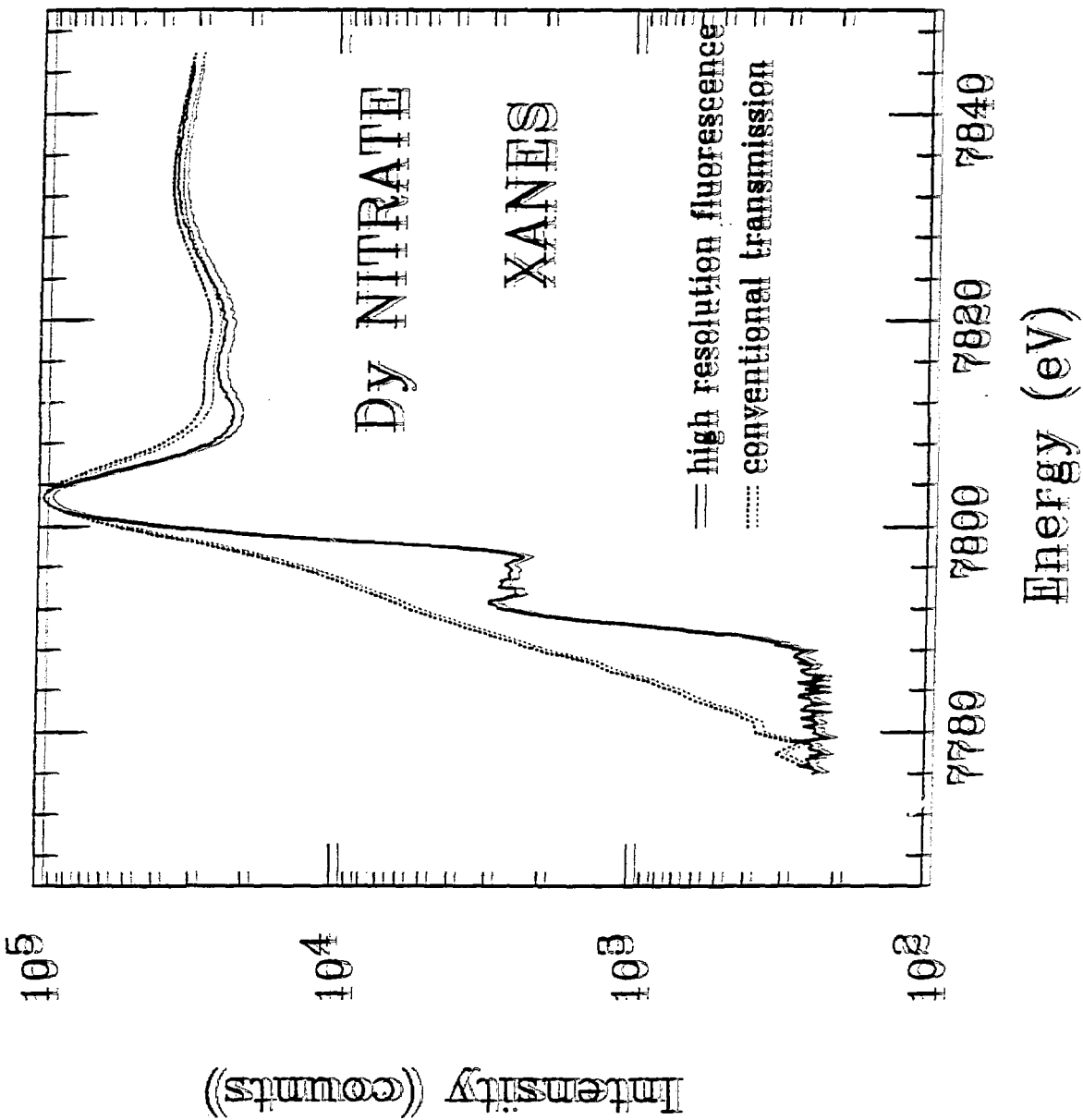
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