

新一代中子灵敏半导体探测器 研究进展

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凝固技术国家重点实验室

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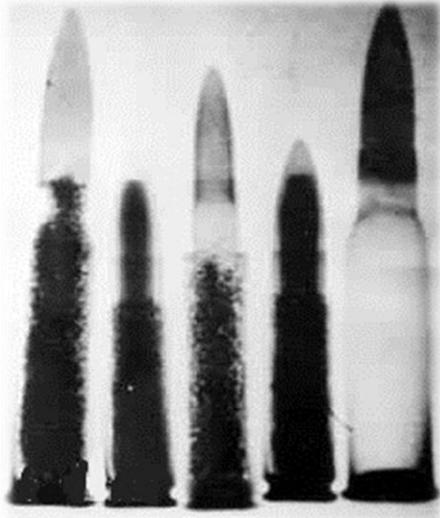
1. 研究背景

2. 研究内容

- CZT热中子探测器
- 基于 ${}^6\text{LiInSe}_2$ 晶体的热中子探测器
- 直接型快中子探测用全有机晶体

3. 结论与展望

1. 研究背景



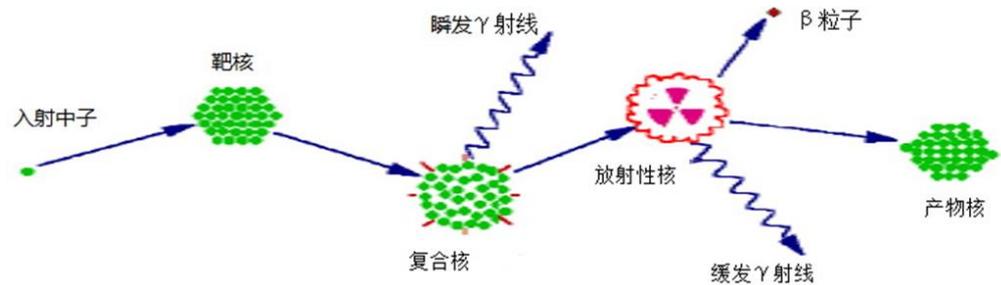
■ Neutron imaging



■ Neutron therapy



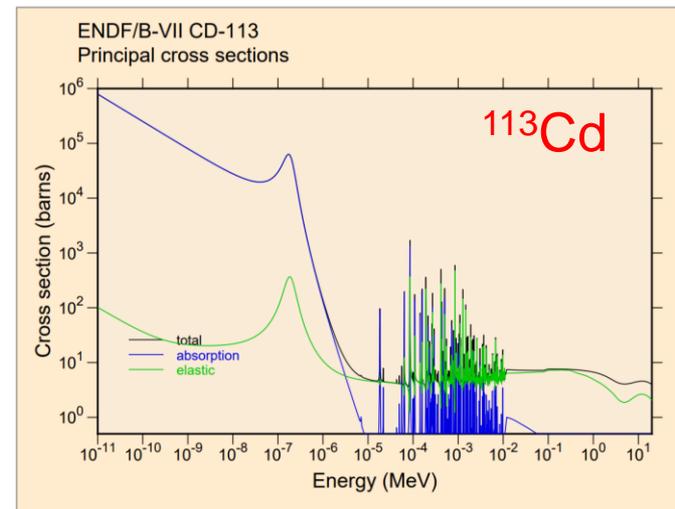
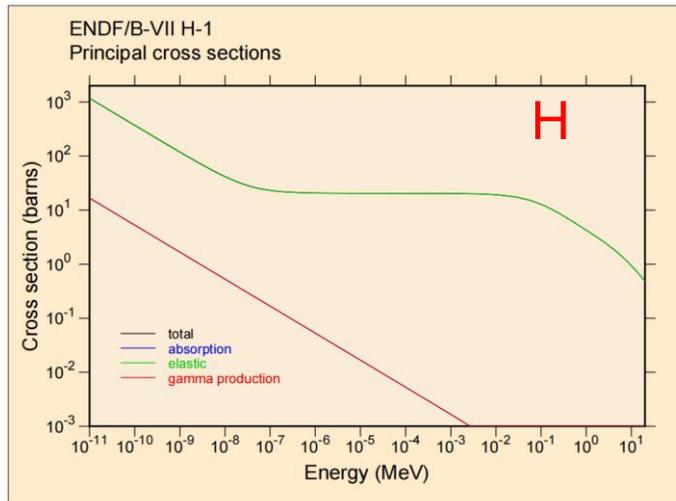
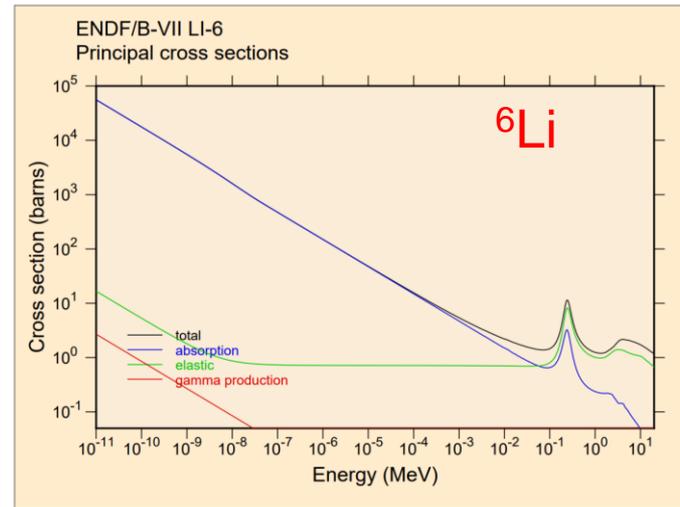
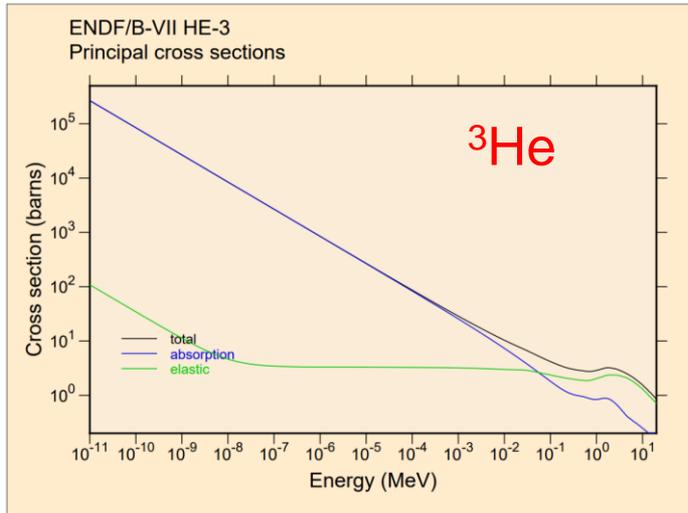
■ Neutron monitor



■ Neutron activation technique

1. 研究背景

典型同位素探测中子的俘获截面

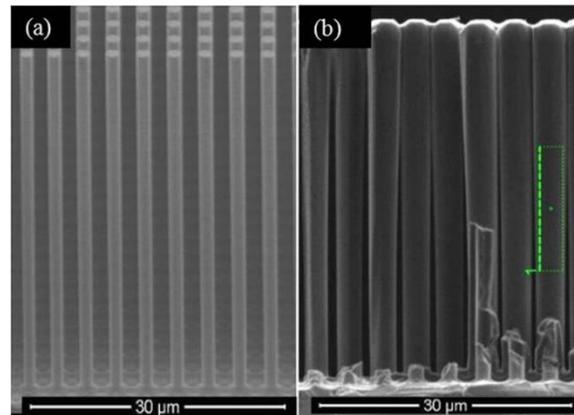
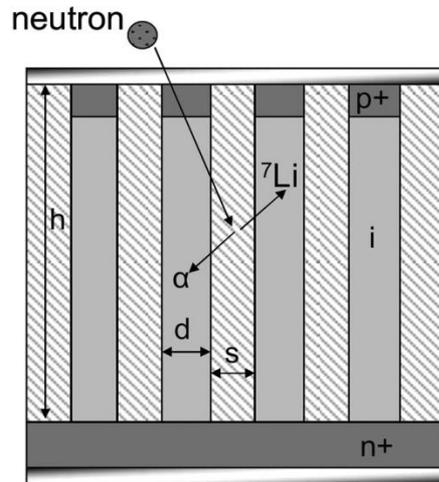
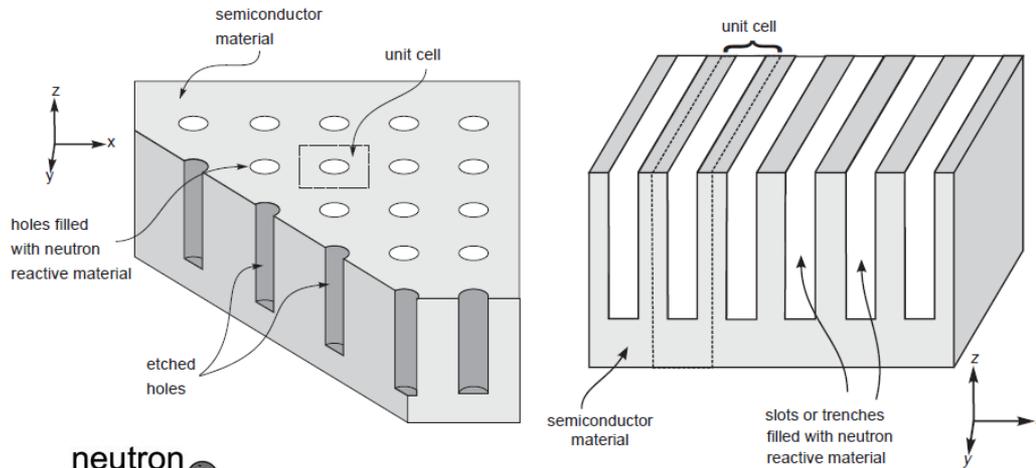


ENDF/B-VII Incident-Neutron Data

<https://t2.lanl.gov/nis/data/endl/endlvii-n.html>

2. 研究背景

■ 半导体+同位素的模式



■ Si wafer + ^6LiF or ^{10}B

McGregor, et al. NIMA: 2009, 606(3): 608.

■ ^{10}B was deposited by CVD on Si wafer

Shao, et al. Applied Physics Letters, 2013, 102(6): 063505.

➤ Thermal neutron detection efficiency of 48.5% using a 50 μm pillar array

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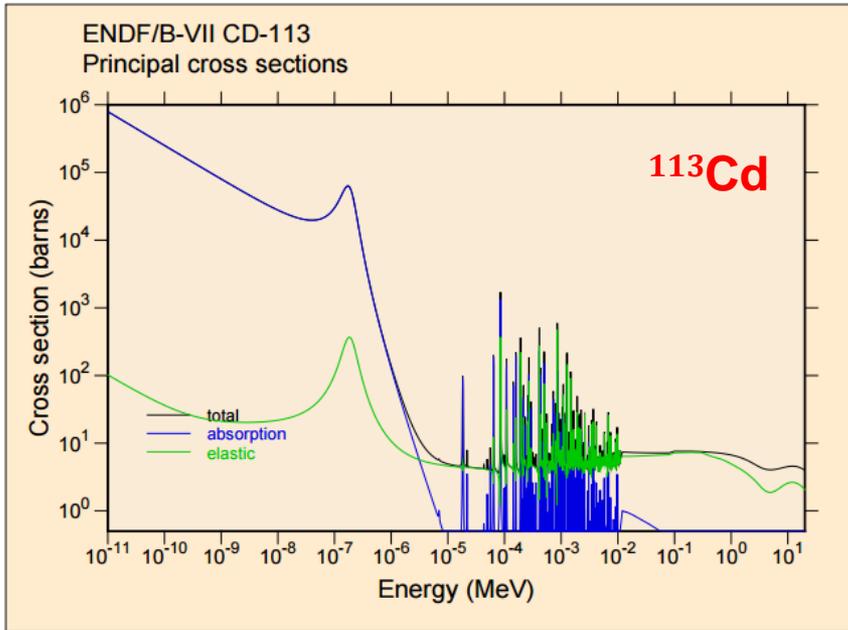
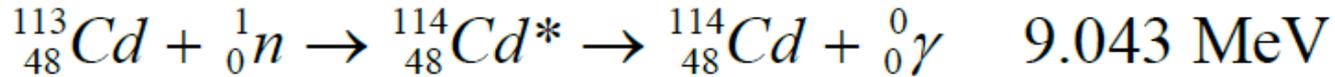
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3. 结论与展望

2.1 CZT热中子探测器

Element (nature Abundance)	³ He (0.00013%)	⁶ Li (7.59%)	¹⁰ B (19.9%)	¹¹³ Cd (12.22%)
Capture cross section for thermal neutron(barns)	5333	940	3837	20600



558 keV (74%)

表 1-5 中子俘获 ¹¹⁴Cd 衰变时放出的 γ 射线能量及所占比重 (>1%)

Table 1-5 Transitions of intensity (>1%) for excited compound ¹¹⁴Cd nucleus as a result of neutron capture.

E (keV)	I (%)								
558.4	74.4	651.2	14.1	805.8	5.11	1364.3	4.64	576.1	4.47
725.3	4.46	1209.7	4.15	1399.6	3.45	5824.6	2.95	1660.4	2.79
2660.1	2.77	1489.6	2.38	1283.5	1.69	2550.1	1.53	654.55	1.33
95.9	1.25	748.39	1.21	2999.7	1.18	707.42	1.16	5433.1	1.16
1305.8	1.14	2767.5	1.14	1826.3	1.10	1370.6	1.08	1301.2	1.03

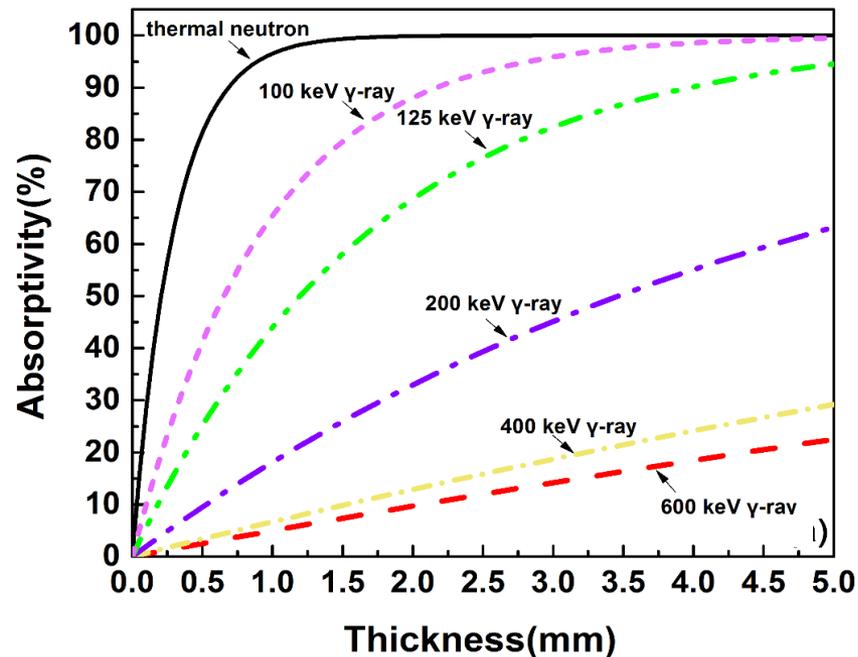
2.1 CZT热中子探测器

■ CdZnTe中子探测器结构设计

热中子吸收: $I(x)/I_0 = e^{-\Sigma x}$

伽马射线在CdZnTe中作用概率: $i = 1 - e^{-\sigma x}$

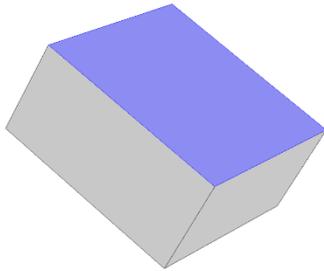
- 90%热中子在探测器表面0.5 mm以内发生核反应
- 558 keV的 γ 射线在探测器内均匀吸收



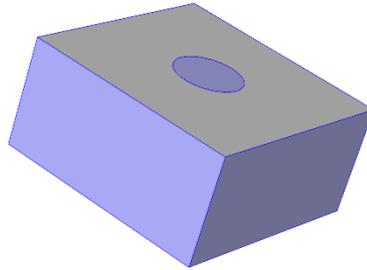
热中子及 γ 射线在CdZnTe晶体中的吸收概率

2.1 CZT热中子探测器

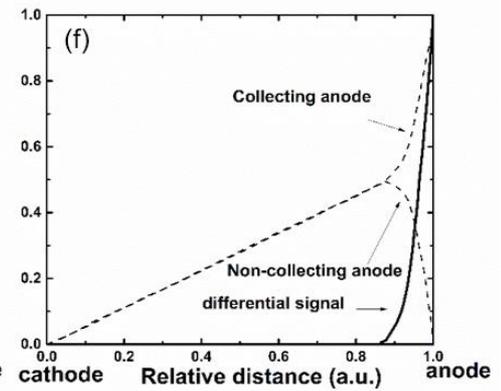
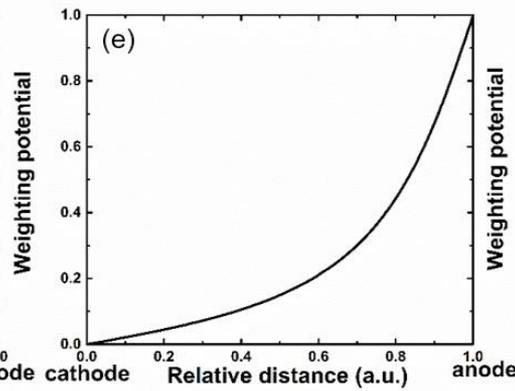
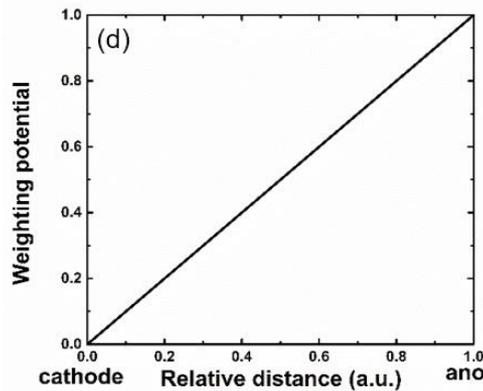
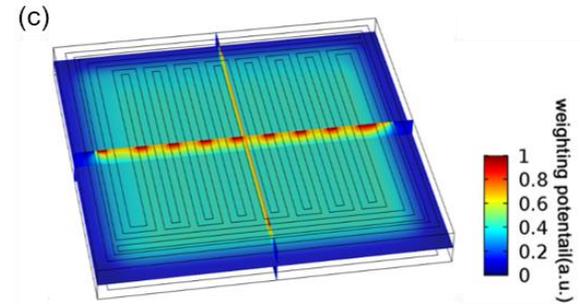
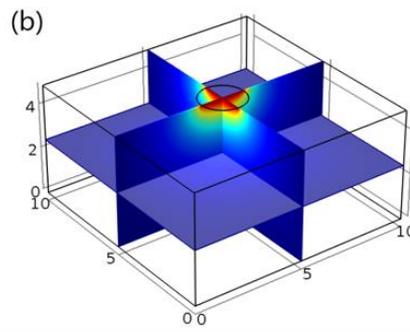
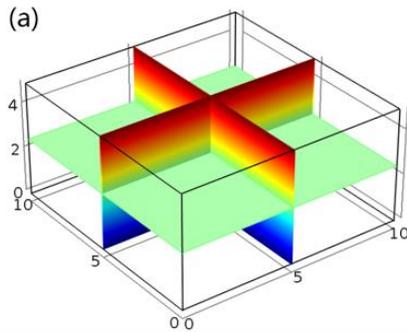
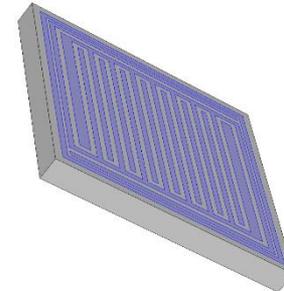
平面型

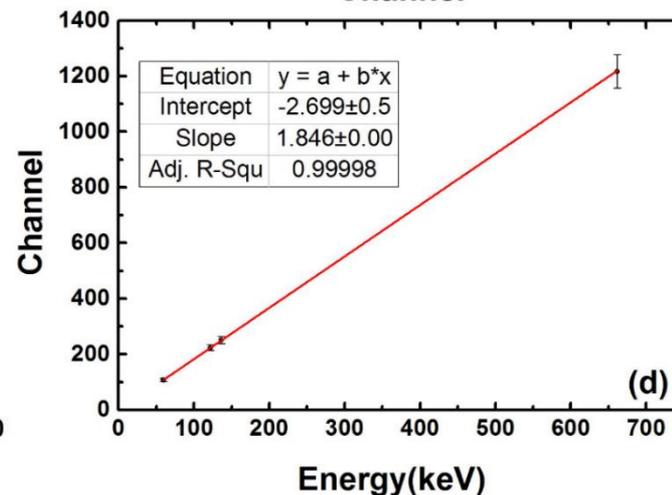
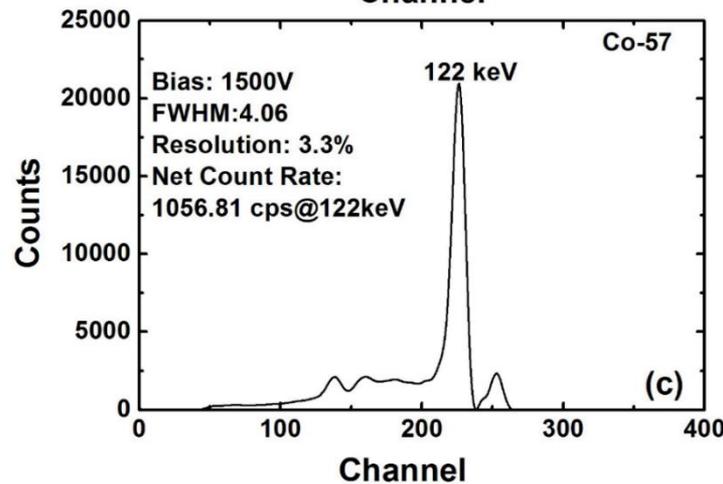
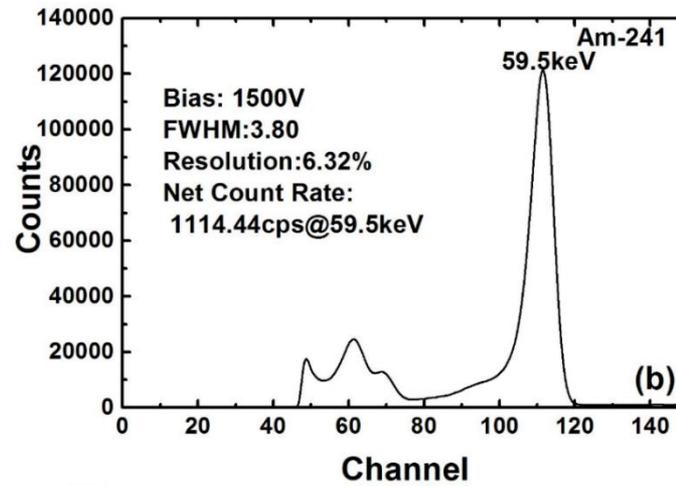
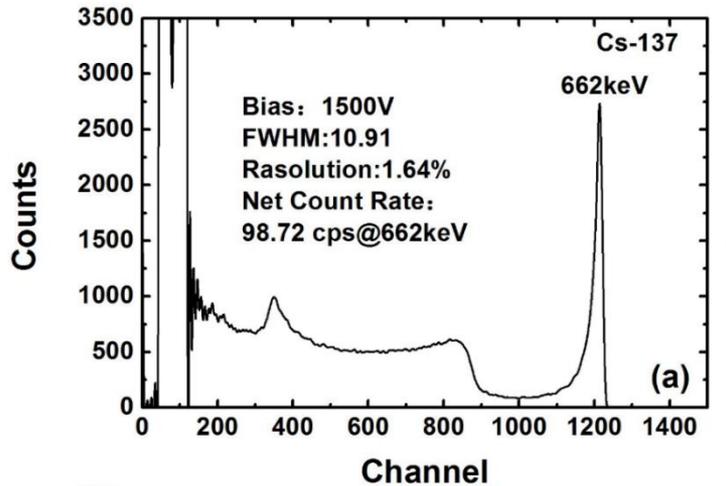


准半球型



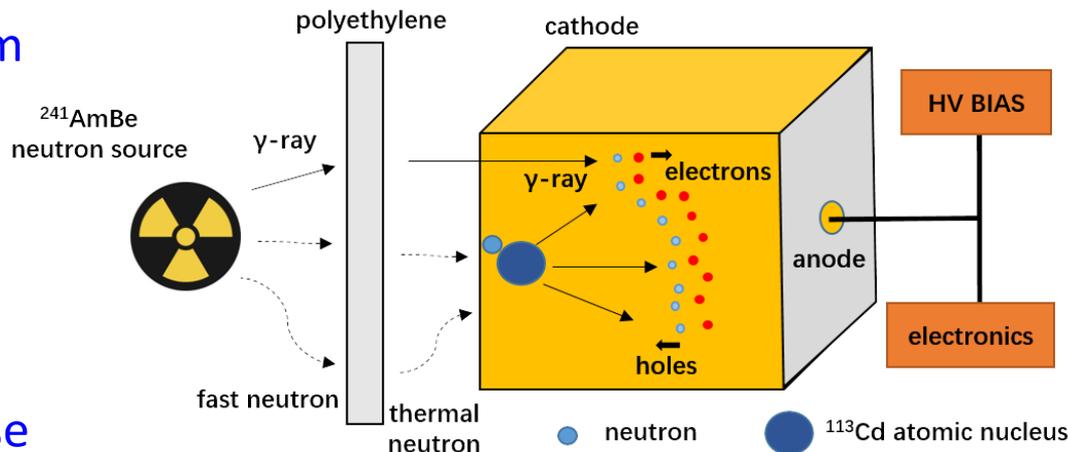
共面栅型



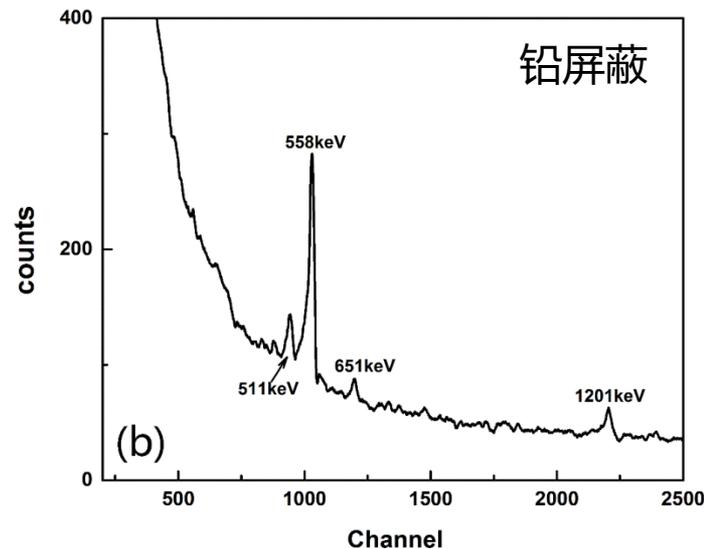
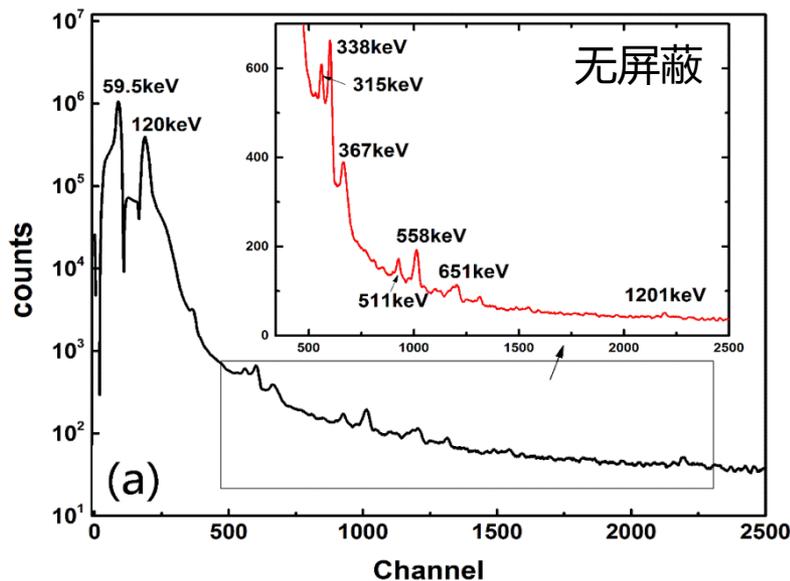


使用 ^{241}Am , ^{57}Co , ^{137}Cs 等 γ 射线源验证探测器能量线性以及确认能量刻度

Schematic diagram



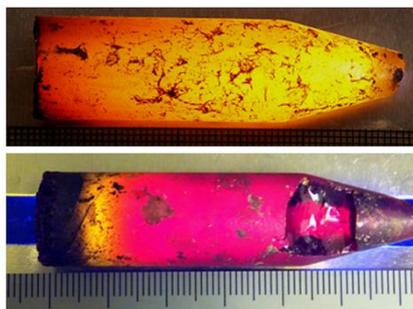
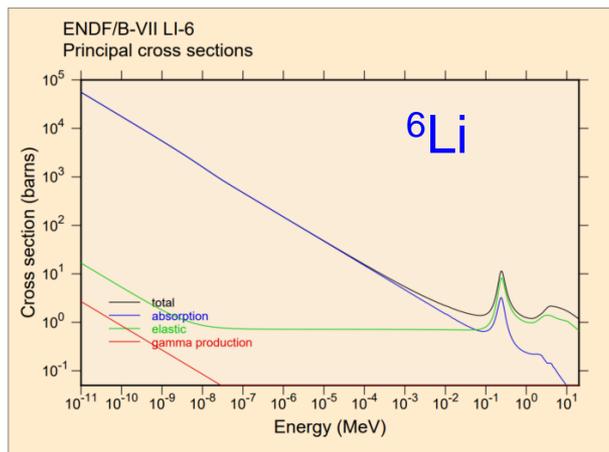
Neutrons response



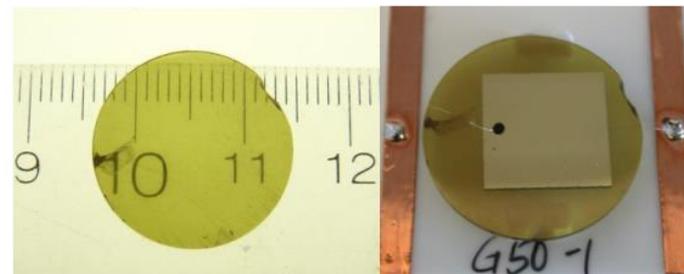
具有高剂量 γ 射线背景下的中子探测能力以及中子/ γ 射线的同时探测能力

2.2 基于 ${}^6\text{LiInSe}_2$ 晶体的热中子探测器

■ 热中子俘获 & 探测



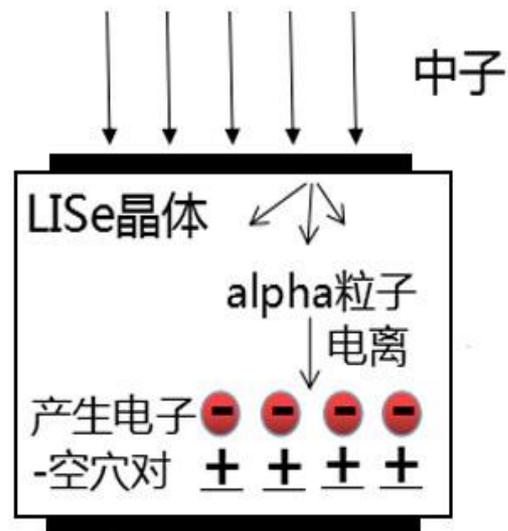
Tupitsyn et al. J. Cryst. Growth, 393 (2014) 23–27



Hard X-Ray, Gamma-Ray, and Neutron Detector Physics XVIII. SPIE, 2016, 9968

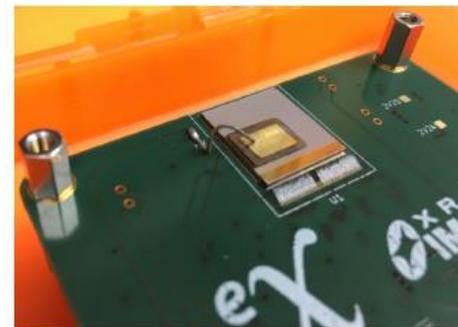
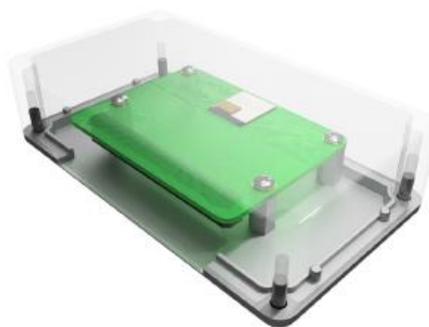
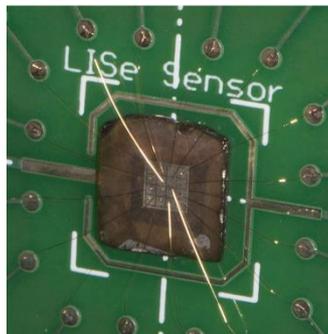
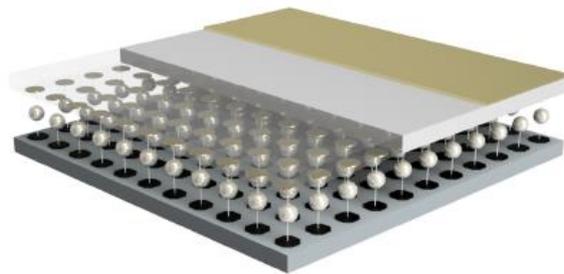
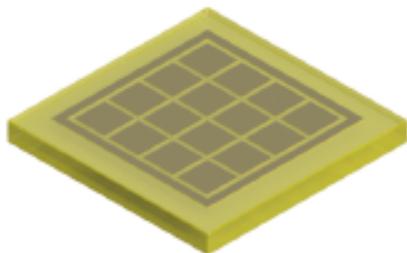


- Both of active layer and detector;
- Large neutron capture cross-section;
- Better n/γ discrimination ability.



2.2 基于 ${}^6\text{LiInSe}_2$ 晶体的热中子探测器

■ LISe中子探测器研制



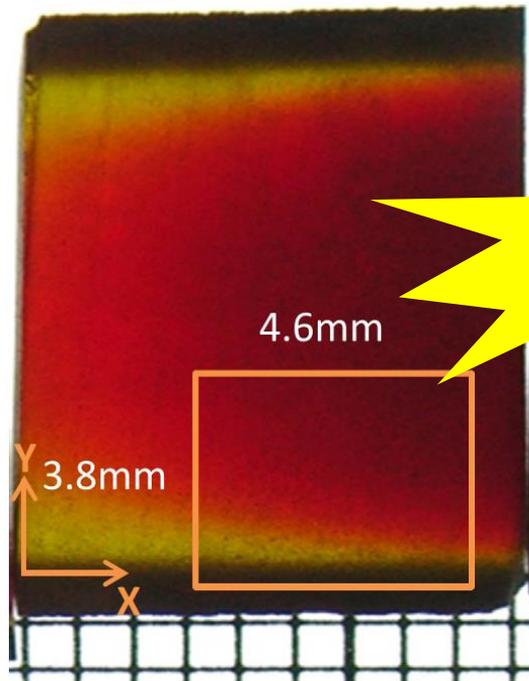
- ◆ 美国橡树岭国家实验室、阿贡国家实验室，田纳西大学、范德堡大学、费斯克大学，RMD公司等单位已进行了初步的战略布局；
- ◆ 并采用 4×4 阵列的LISe探测器尝试进行热中子成像，空间分辨率达到 $300 \mu\text{m}$ ，结合ASIC读出电路，实现了热中子位置分辨小于 $200 \mu\text{m}$

Nucl. Instrum. & Meth. A, 2016, 833: 142. & J. Imaging, 2018, 4: 10.

2.2 基于 ${}^6\text{LiInSe}_2$ 晶体的热中子探测器

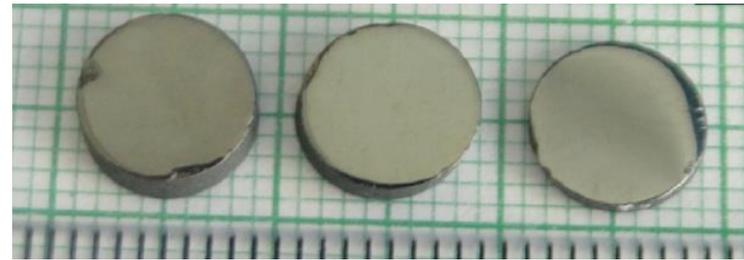
■ VB method from a melt

Melting point: 900-920 ° C

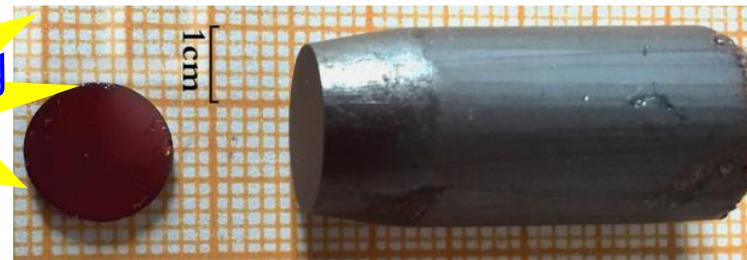


Inhomogeneity

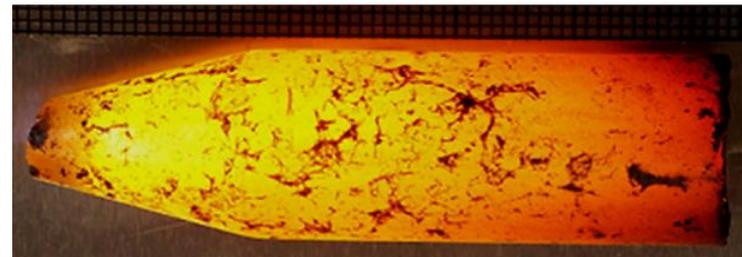
Hard X-Ray, Gamma-Ray, and Neutron
Detector Physics XV. SPIE, 2013,
8852.



Journal of Crystal Growth, 2014, 388:17-21.



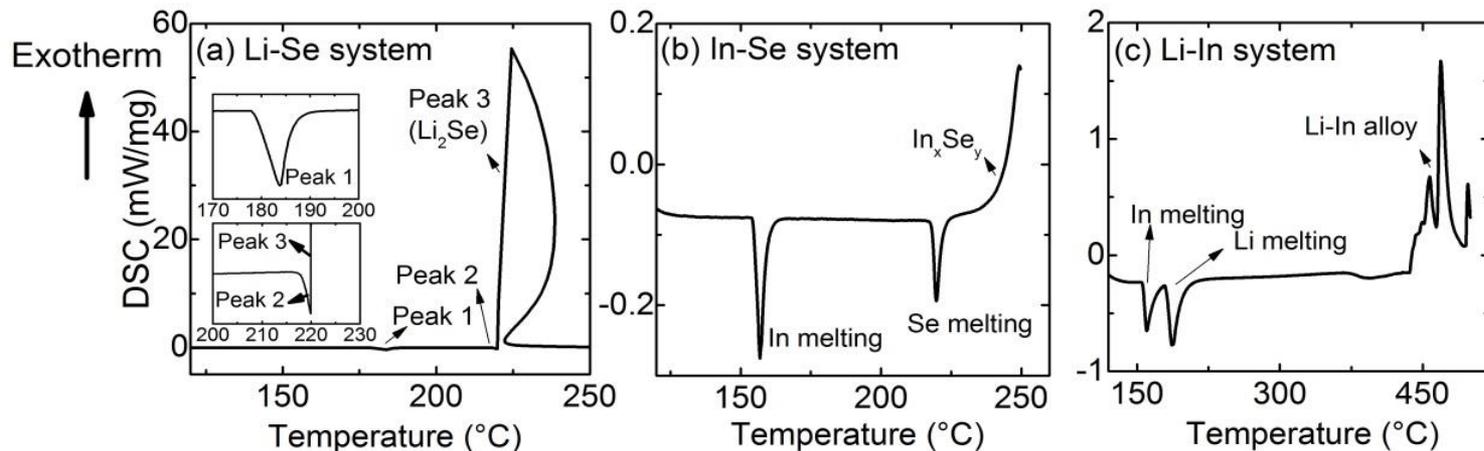
Journal of Crystal Growth, 2000, 218:313-322.



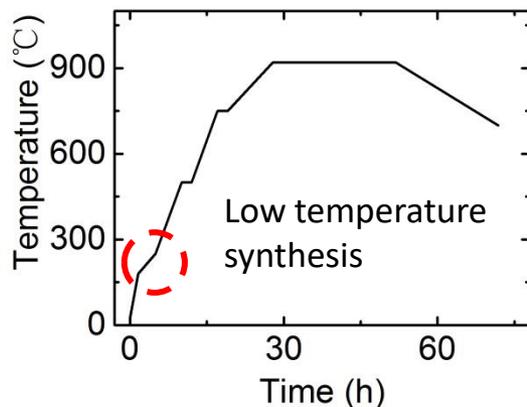
Journal of Crystal Growth, 2014, 393:23-27.

2.2 基于 ${}^6\text{LiInSe}_2$ 晶体的热中子探测器

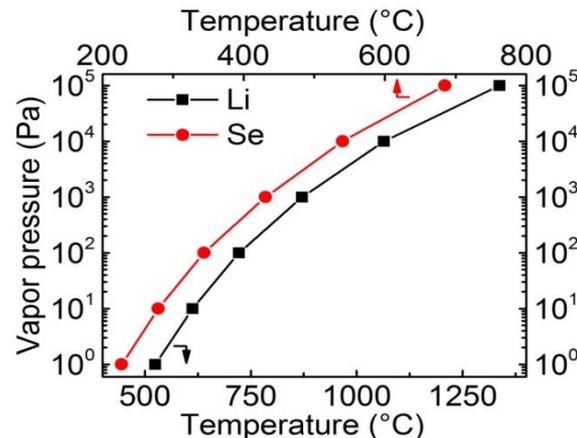
➤ Li-In-Se reaction (DSC)



■ Set up of temperature profile



■ Reduce stoichiometric deviation

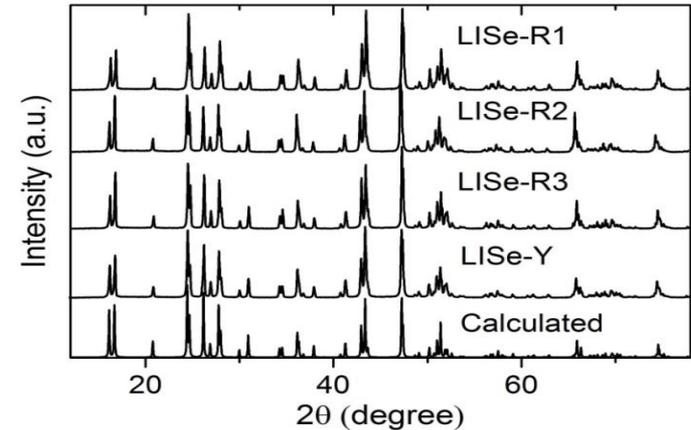


2.2 基于 ${}^6\text{LiInSe}_2$ 晶体的热中子探测器

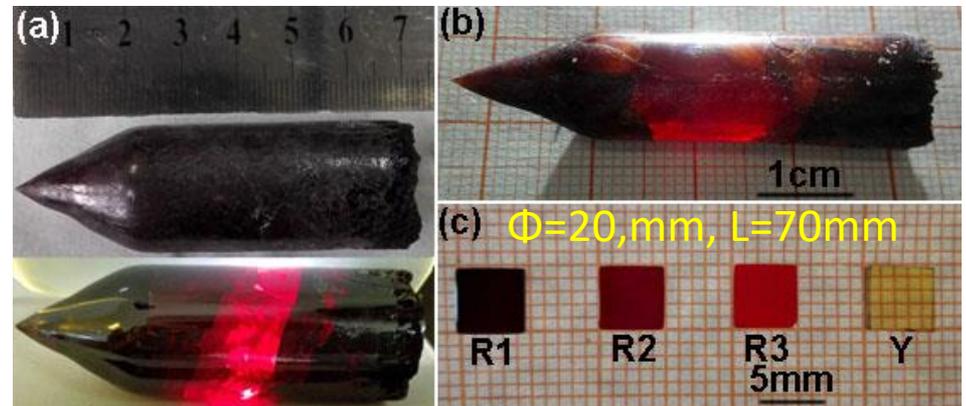
➤ Synthesis using different crucible



■ PXRD



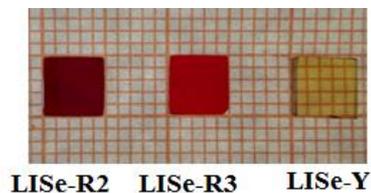
No.	Excess Li and Se	Composition	Crucible
LISe-R1	5% Li+3% Se	$\text{Li}_{0.99}\text{In}_{1.02}\text{Se}_2$	SiO_2
LISe-R2	5% Li+2% Se	$\text{Li}_{1.04}\text{In}_{1.10}\text{Se}_2$	SiO_2
LISe-R3	3% Li+2% Se	$\text{Li}_{0.99}\text{In}_{1.02}\text{Se}_2$	SiO_2
LISe-Y	3% Li+2% Se	$\text{LiIn}_{1.06}\text{Se}_2$	Graphite



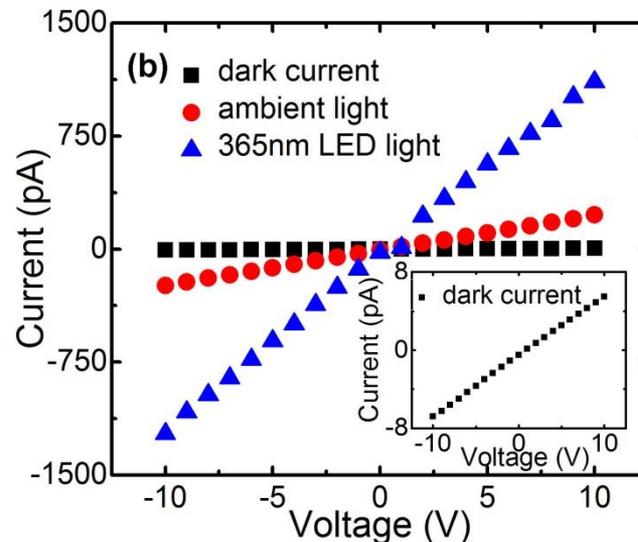
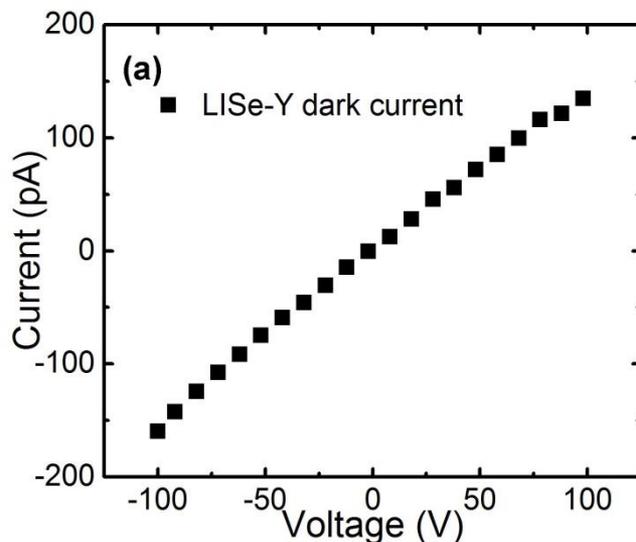
2.2 基于 ${}^6\text{LiInSe}_2$ 晶体的热中子探测器

■ Device fabrication

■ I-V curves



Planar detector



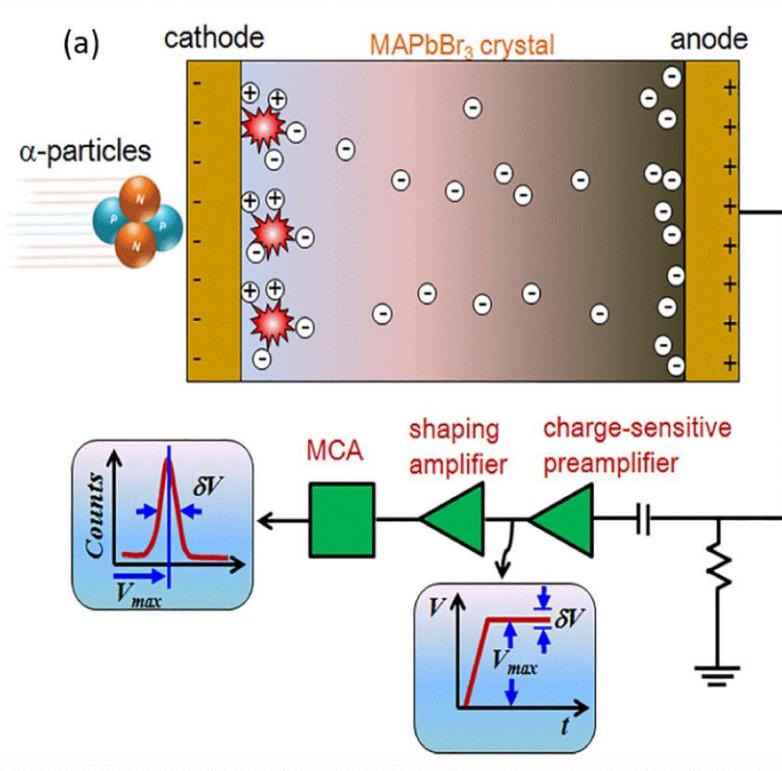
$$I = \frac{SV}{L\rho}$$

➤ Resistivity is on the order of 10^{11} - $10^{12} \Omega\cdot\text{cm}$;

$$\sigma_{\text{photo}}/\sigma_{\text{dark}}$$

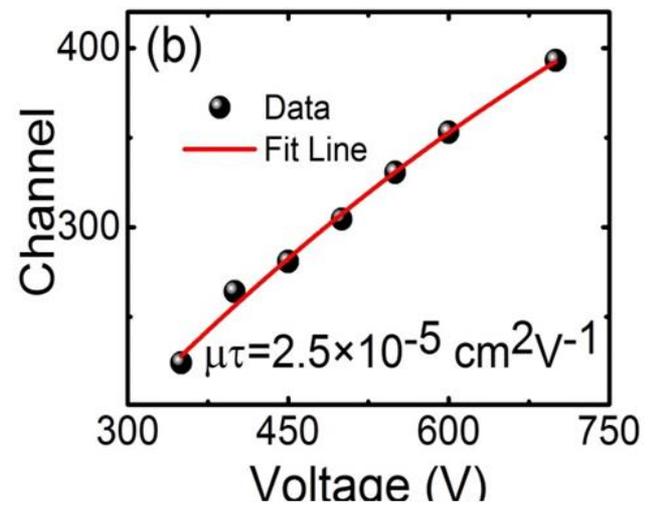
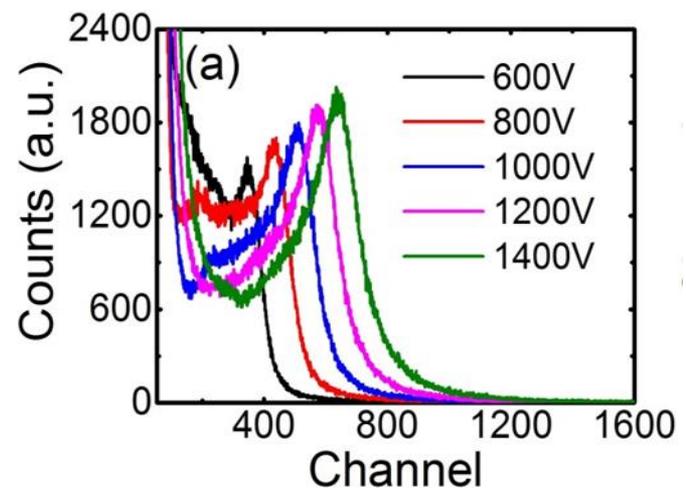
➤ The ONN-OFF ratio is in the range of 150-200

2.2 基于 ${}^6\text{LiInSe}_2$ 晶体的热中子探测器



$$CCE \approx \frac{\mu\tau V}{d^2} \left[1 - \exp\left(-\frac{d^2}{\mu\tau V}\right) \right] \quad \text{--- Hecht equation}$$

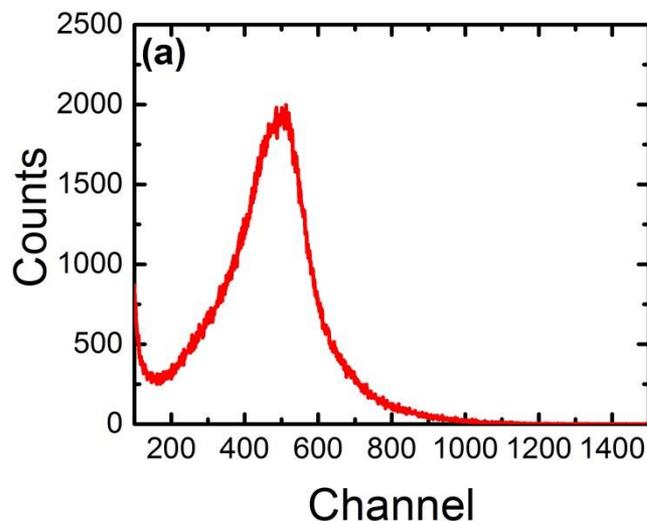
➤ $\mu\tau$ value of LiInSe_2 is on the order $10^{-5} \text{ cm}^2/\text{V}$.



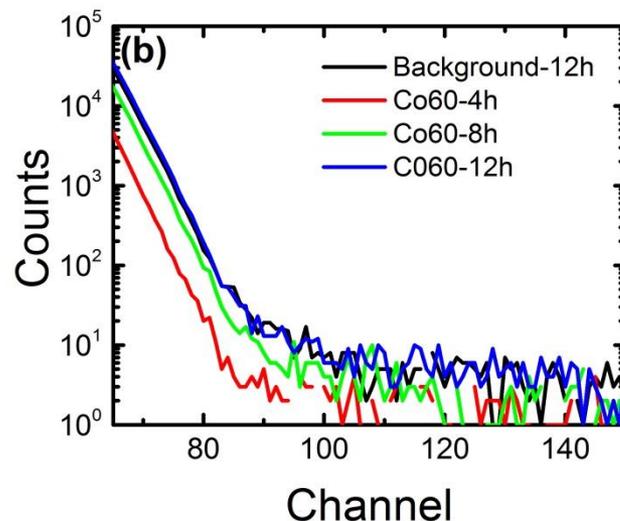
L. Guo, et al. *Cryst. Growth Des.* 2018, 18(5): 2864-2870.

2.2 基于 ${}^6\text{LiInSe}_2$ 晶体的热中子探测器

■ ${}^{241}\text{Am}$ @ 5.48 MeV



■ ${}^{60}\text{Co}$ @ 1.33 MeV



Wafer	Formula	E_g /eV	Resolution	$\mu\tau_e$ / cm^2V^{-1}
LISe-R2	$\text{Li}_{1.04}\text{In}_{1.10}\text{Se}_2$	2.01	43.1%	9.3×10^{-6}
LISe-R3	$\text{Li}_{0.99}\text{In}_{1.02}\text{Se}_2$	2.15	28.9%	1.5×10^{-5}
LISe-Y	$\text{LiIn}_{1.06}\text{Se}_2$	2.83	23.3%	2.5×10^{-5}
Ref.[1]	$\text{Li}_{0.91}\text{InSe}_2$	2.83	38.2%	7.9×10^{-6}

[1] Hard X-Ray, Gamma-Ray, and Neutron Detector Physics XV. SPIE, 2014, 9213.

2.3 快中子探测用全有机晶体

快中子的特点与应用

快中子 \longrightarrow 弹性散射、核反应
能量 $> 0.5\text{MeV}$ 穿过重元素、被轻元素吸收

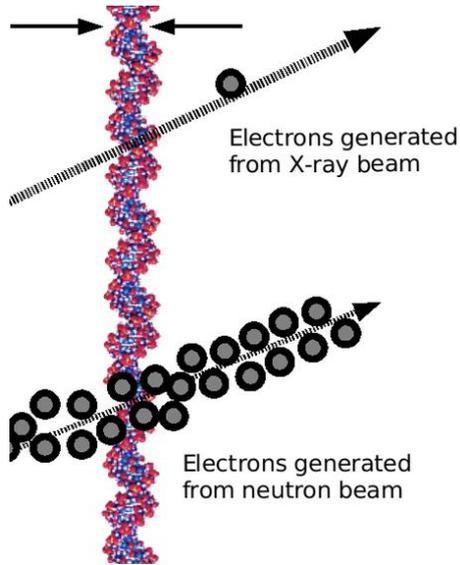
$$\sigma \propto \frac{4Z}{(Z+1)^2}$$



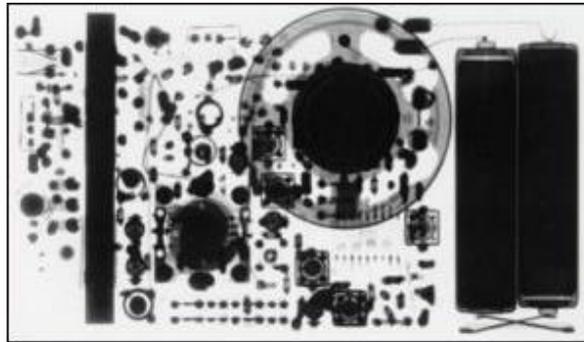
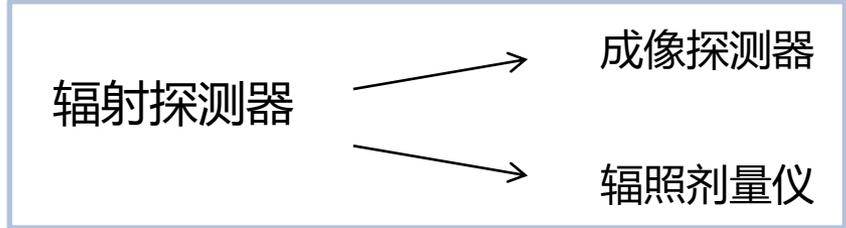
核能生产



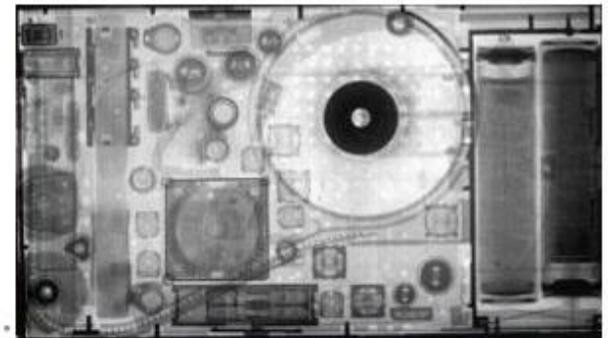
核武器



肿瘤放疗



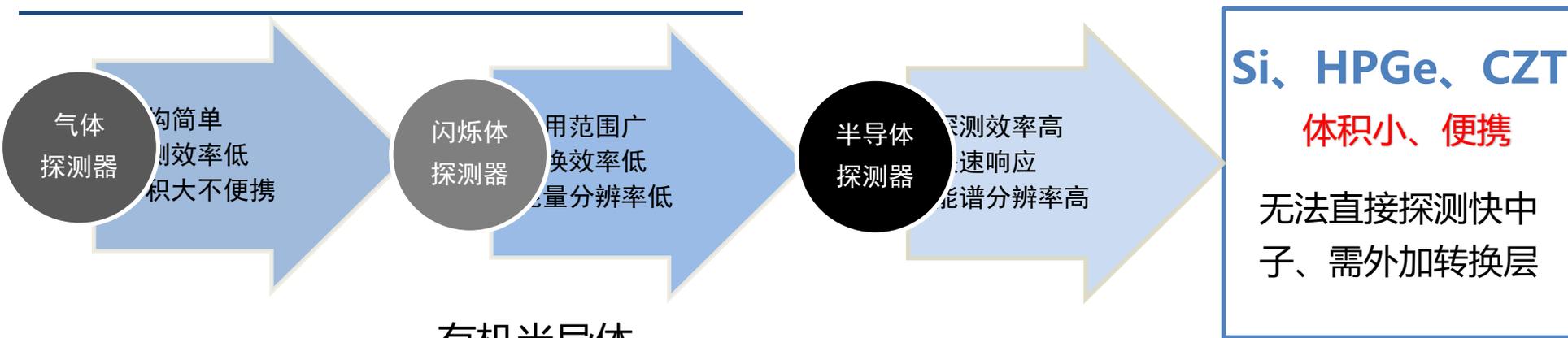
X射线成像



中子成像

2.3 快中子探测用全有机晶体

半导体快中子探测器



有机半导体

低原子序数

低温溶液法制备

低成本

快中子探测

- ✓ 中子吸收效率高
- ✓ 小体积、便携
- ✓ 直接探测

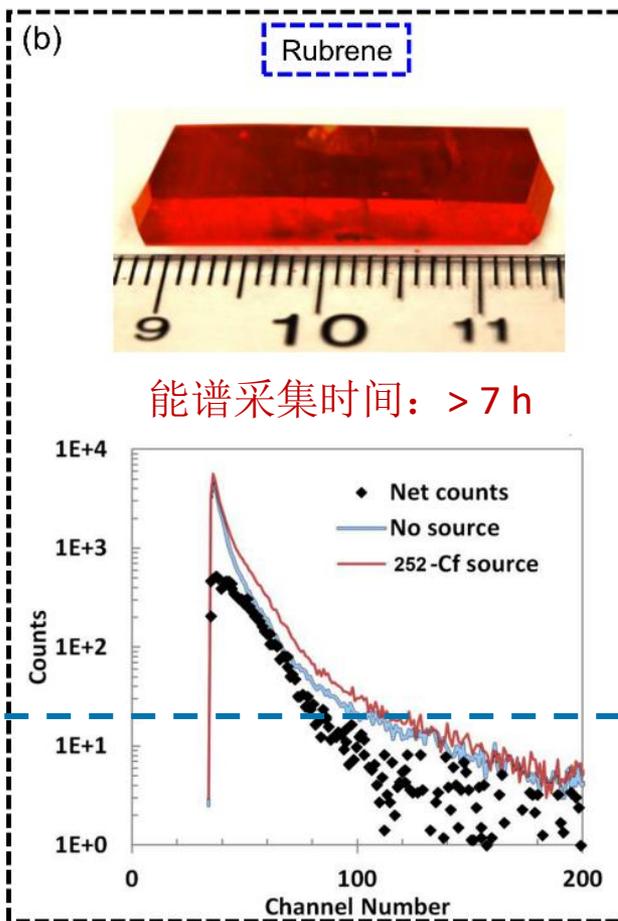
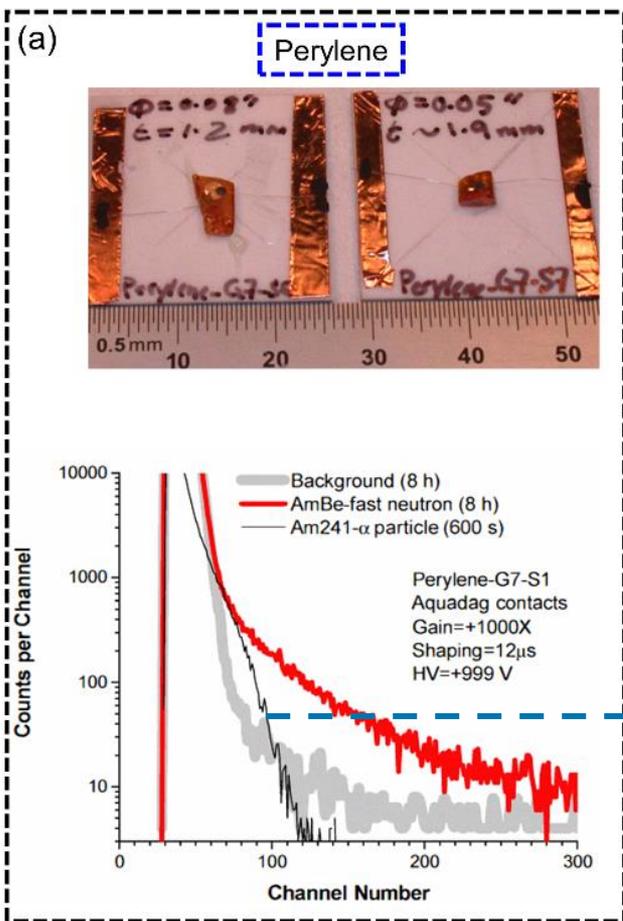
低迁移率、低载流子收集效率

对半导体核辐射探测材料的要求：

较高的吸收效率；
较大的禁带宽度；
室温下较高的电阻率 (ρ) ；
较高的载流子迁移率(μ)。

探索高电输运性能有机半导体应用于快中子的直接探测

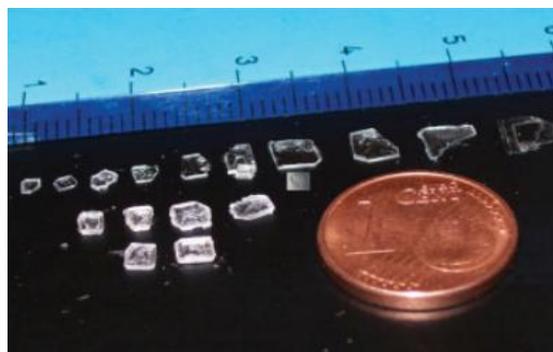
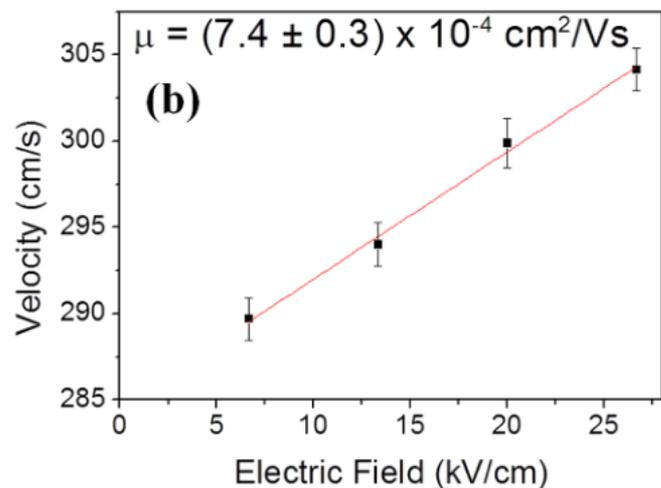
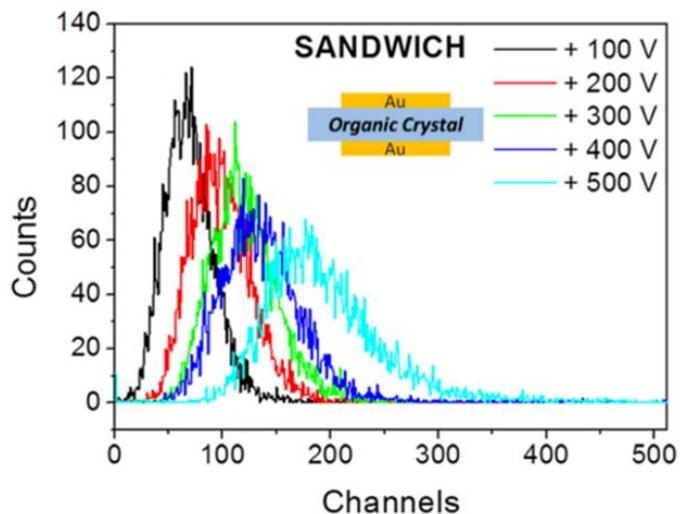
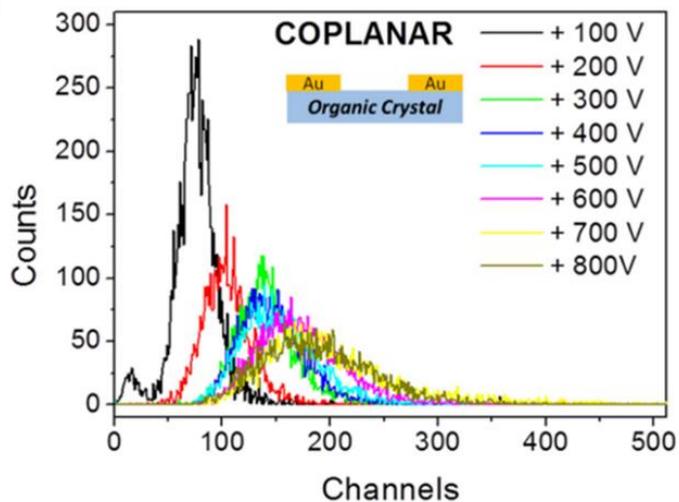
直接型快中子探测器需要同时满足：高氢密度及**优异的带电粒子探测能力**



直接型快中子探测器现状

- 材料种类有限
- 探测及中子辐照机理缺失
- 探测效率低
- 响应时间极慢
- 无能量识别能力
- 信号干扰大

➤ 带电粒子探测能力差

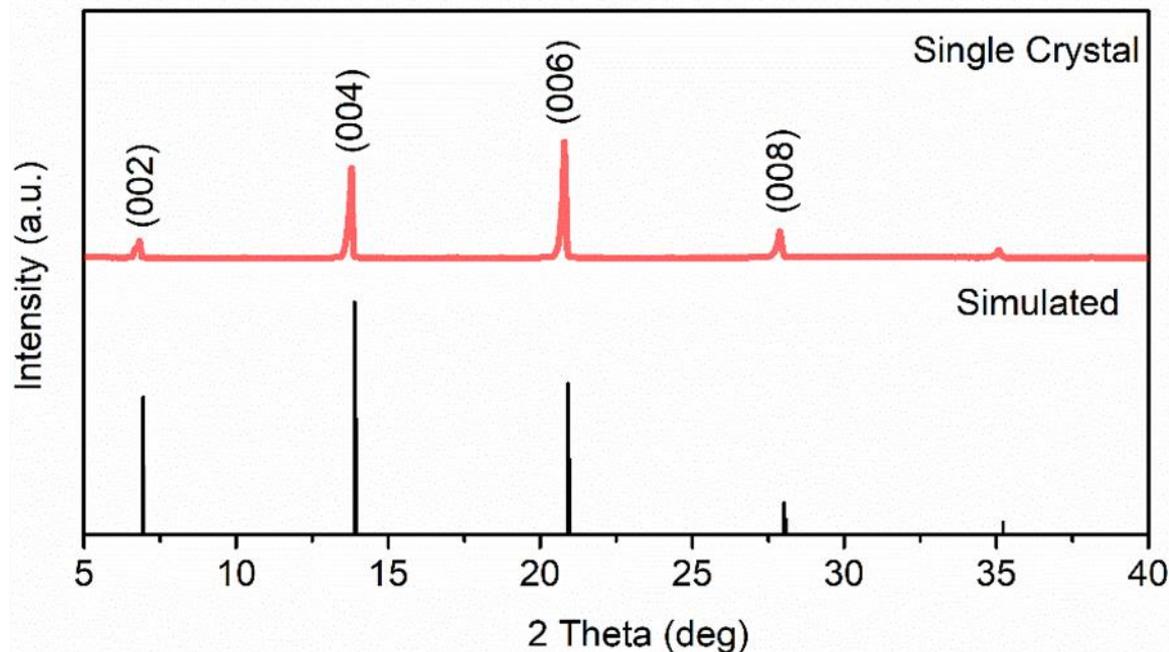
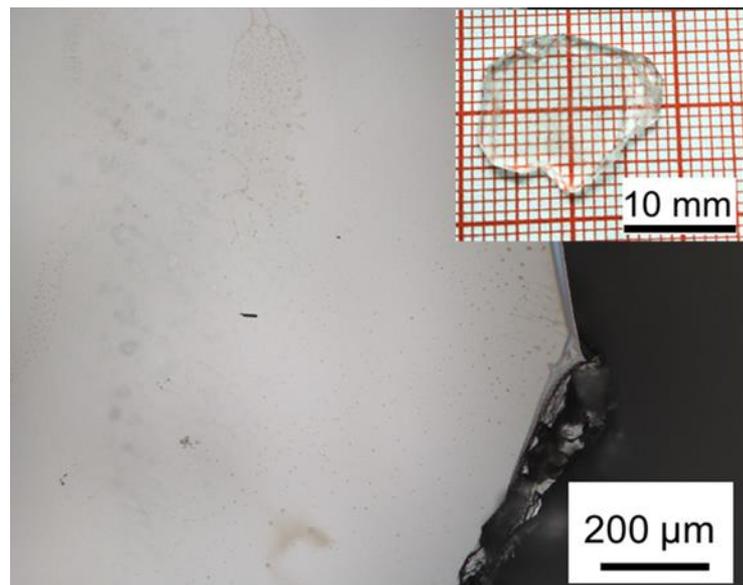


- 灵敏体积小
- 生长缺陷多
- 载流子迁移率低
- 电荷收集效率差

良好的带电粒子探测，但尚未实现快中子探测

2.3.1 基于4HCB有机半导体的直接型快中子探测

生长态4HCB(四羟基苯甲氰)单晶结构表征

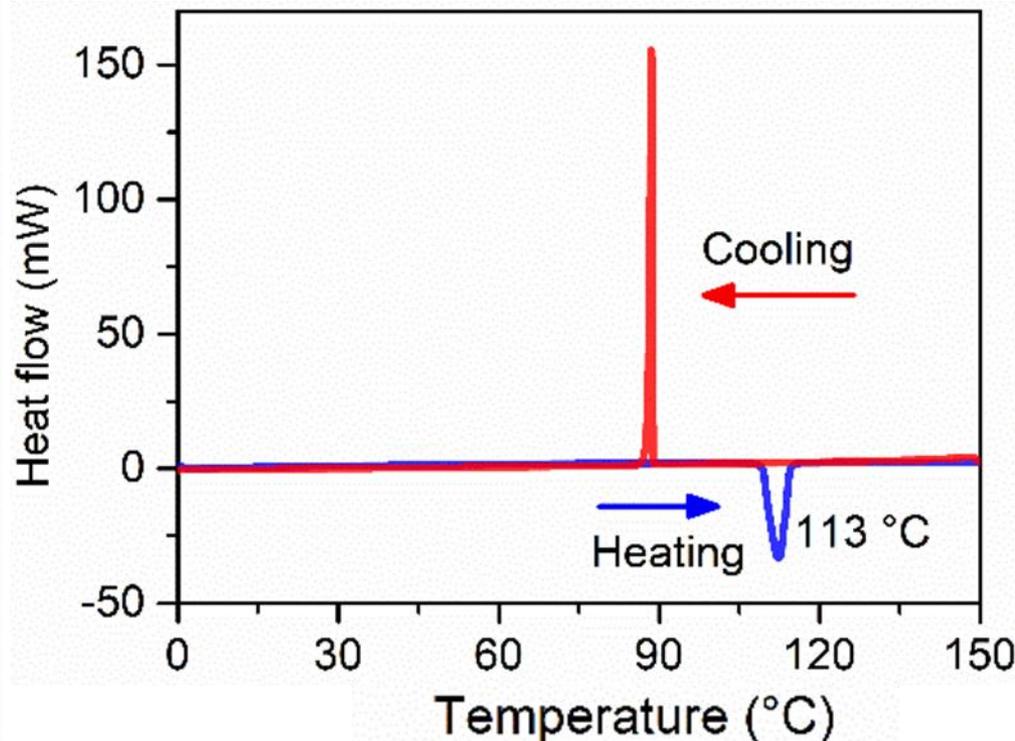
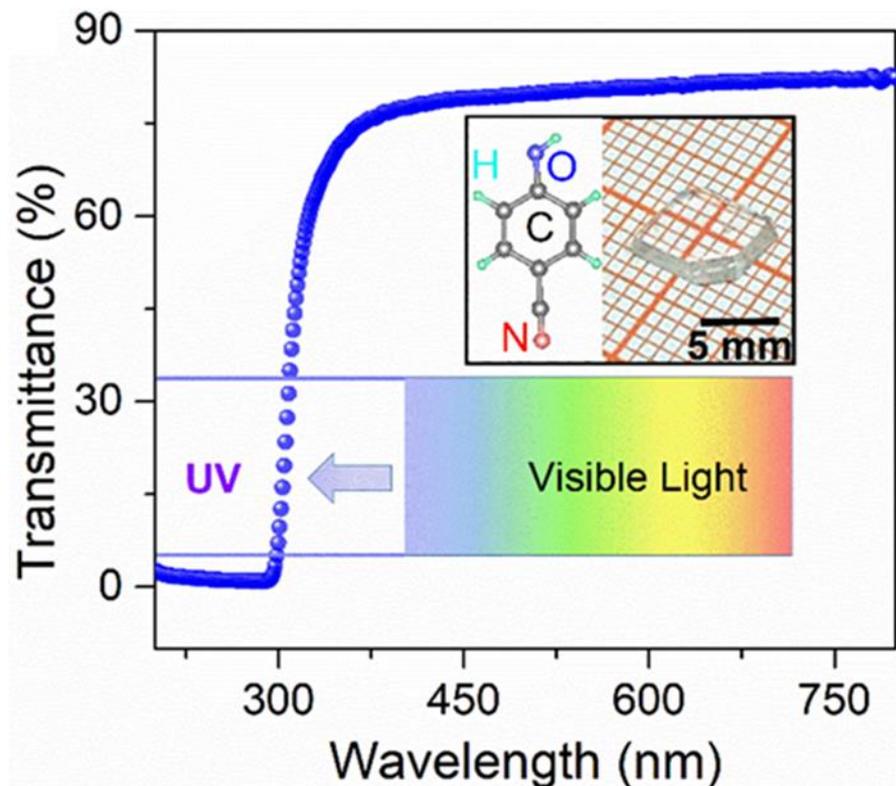


- ✓ 大尺寸4HCB单晶~ $18 \times 15 \times 1.2 \text{ mm}^3$
- ✓ 表面缺陷密度低

- ✓ 最大暴露面为 (001) 晶面

2.3.1 基于4HCB有机半导体的直接型快中子探测

生长态4HCB单晶光学及热稳定性表征

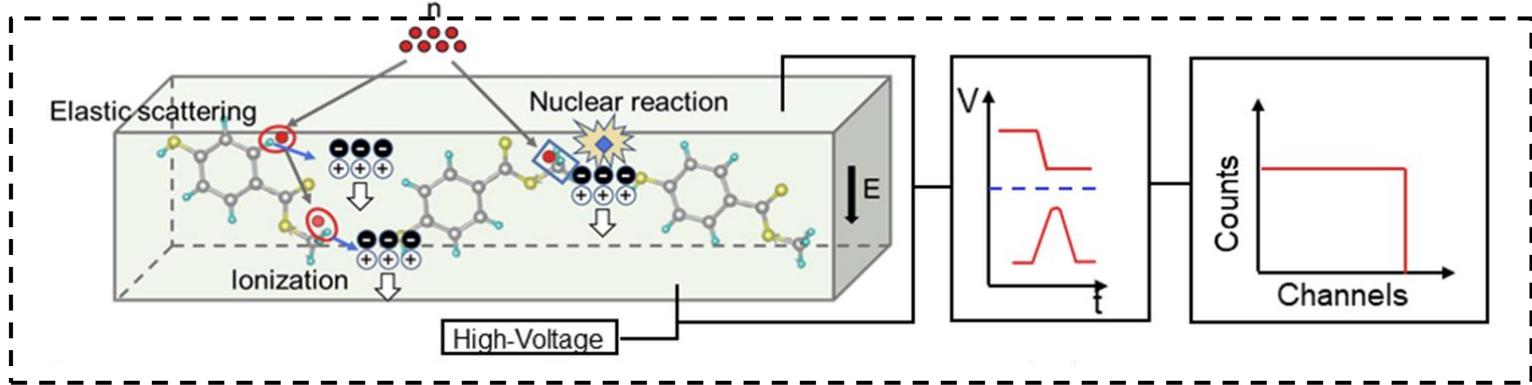


4HCB单晶 探测器

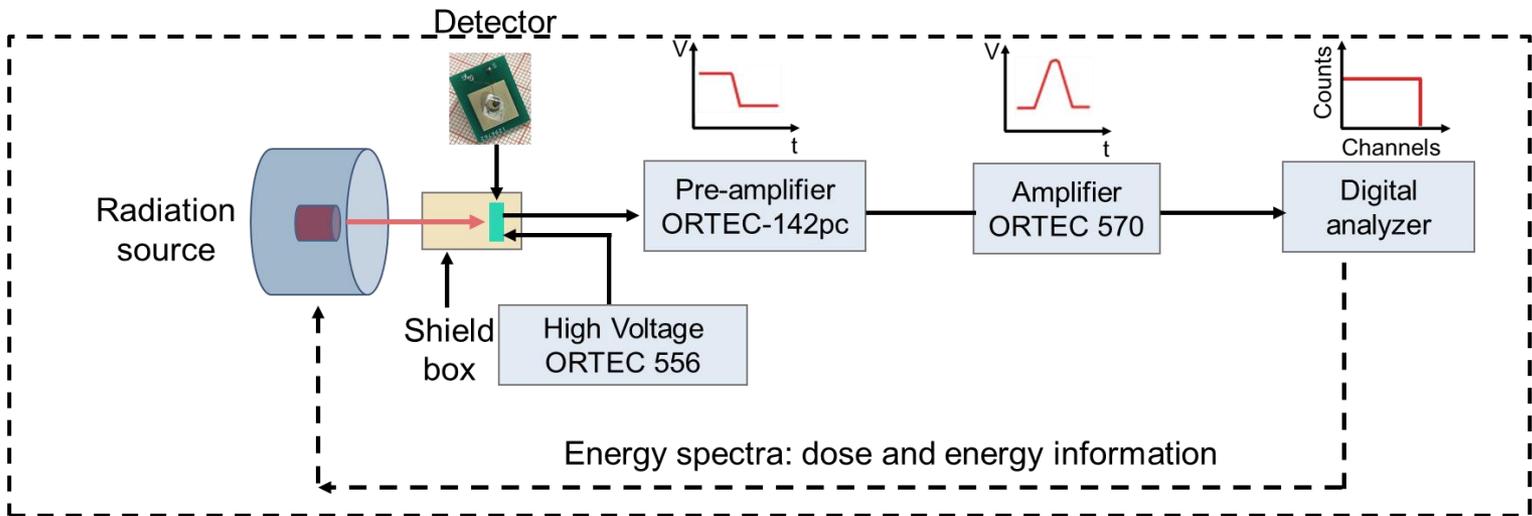
- ✓ 厘米尺寸 —— 探测效率高
- ✓ 缺陷密度低 —— 电输运性能好、光生载流子载流子复合概率低
- ✓ 热稳定性好 —— 无结构相变所致的器件失稳问题
- ✓ 禁带宽度大 (4.08 eV) —— 暗电流低、可见光不敏感、耐辐照能力强

2.3.1 基于4HCB有机半导体的直接型快中子探测

直接型中子探测原理

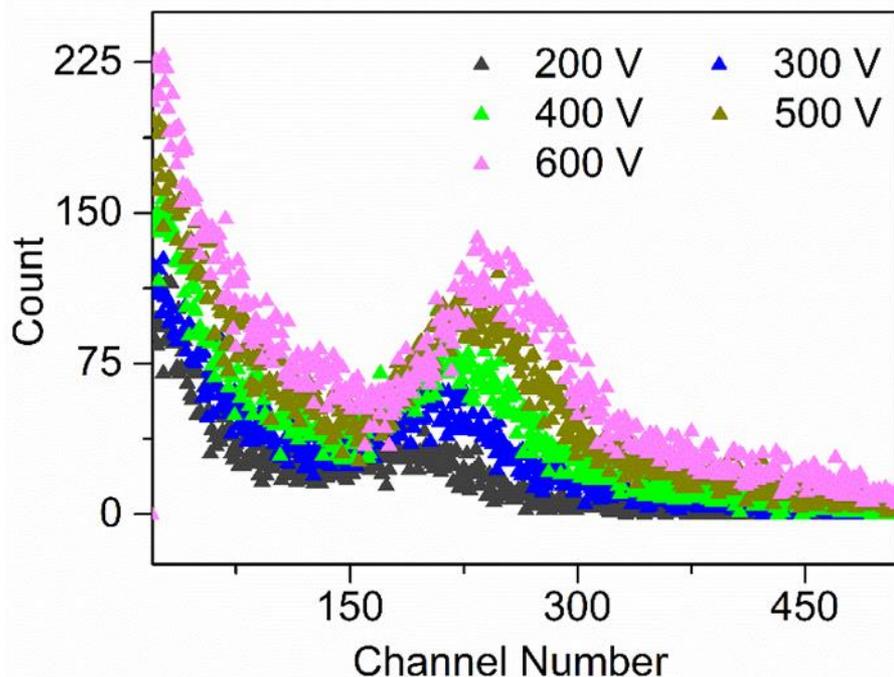


脉冲法探测系统

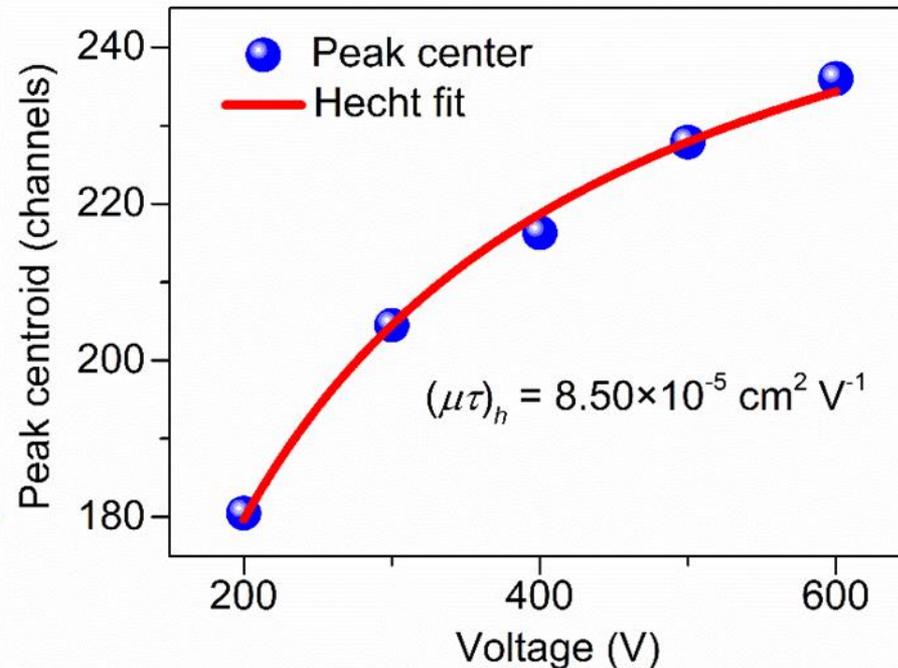


2.3.1 基于4HCB有机半导体的直接型快中子探测

4HCB探测器的带电粒子探测能力



全能峰分辨率 45%



$(\mu\tau)_h = 10^{-4} \sim 10^{-5} \text{ cm}^2 \text{ V}^{-1}$

文献报道: $10^{-6} \text{ cm}^2 \text{ V}^{-1}$

Appl. Phys. Lett., 2016, 108: 153301.

2.3.1 基于4HCB有机半导体的直接型快中子探测

4HCB 探测器与快中子的相互作用效率

$$n_r = I \times n_l \times \sigma \times V$$

σ 为反应截面, I 是入射中子注量率, n_l 是氢核密度

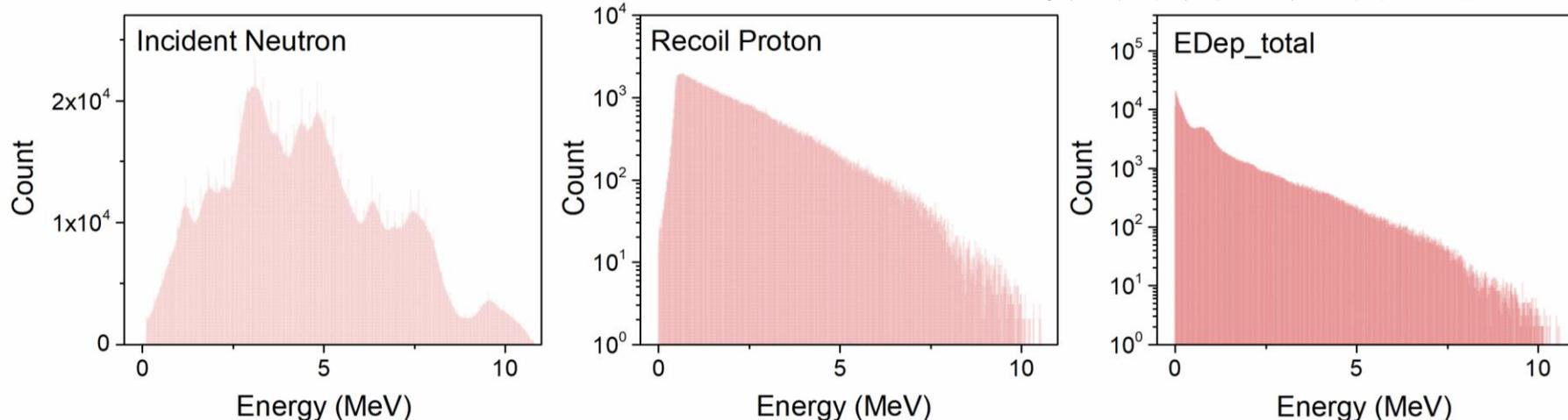
10 MeV 的快中子, $\sigma(\text{H}) = 1 \text{ b}$ ($1 \text{ b} = 10^{-24} \text{ cm}^2$)

4HCB 单晶, $n_l(\text{H}) = 3.2 \times 10^{22} \text{ cm}^{-3}$, 体积为 0.1 cm^3 的探测器

单位中子与 H 核的弹性碰撞数目为 $3.2 \times 10^{-3} \text{ n s}^{-1}$

Geant4模拟: 0.1 cm^3 的4HCB探测器中子能量沉积谱

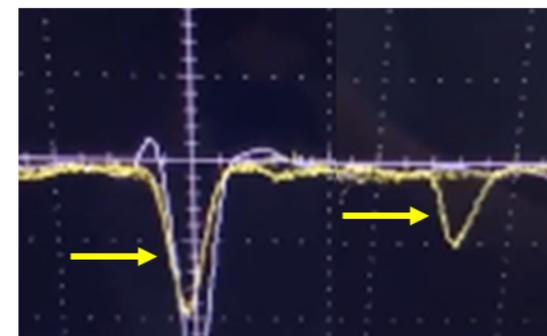
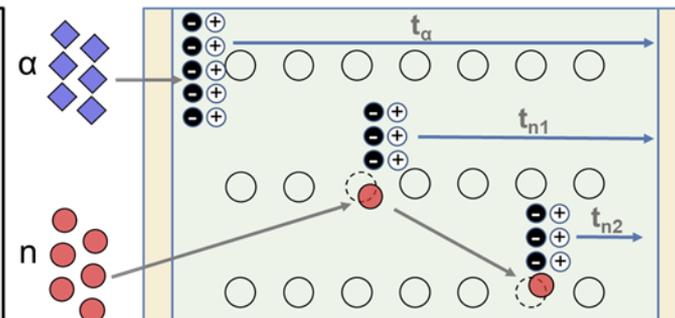
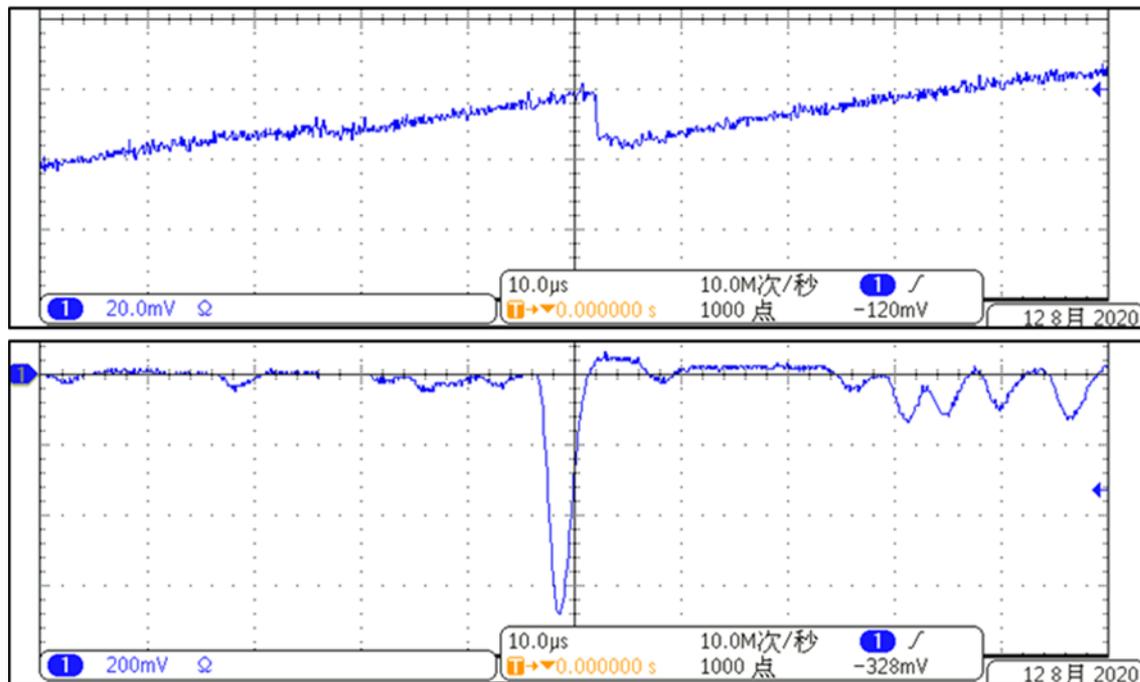
(探测效率及能量分辨率的定义)



2.3.1 基于4HCB有机半导体的直接型快中子探测

4HCB探测器对中子的脉冲响应

中子响应时间定义



脉冲幅度大小不一



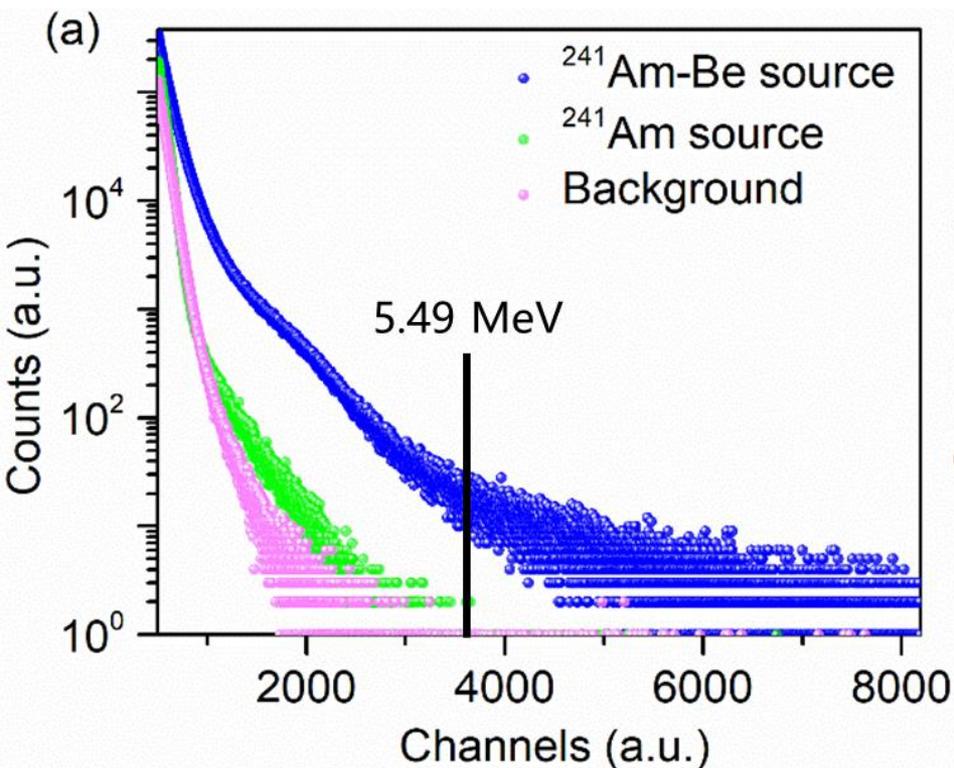
反冲质子能量、位置随机



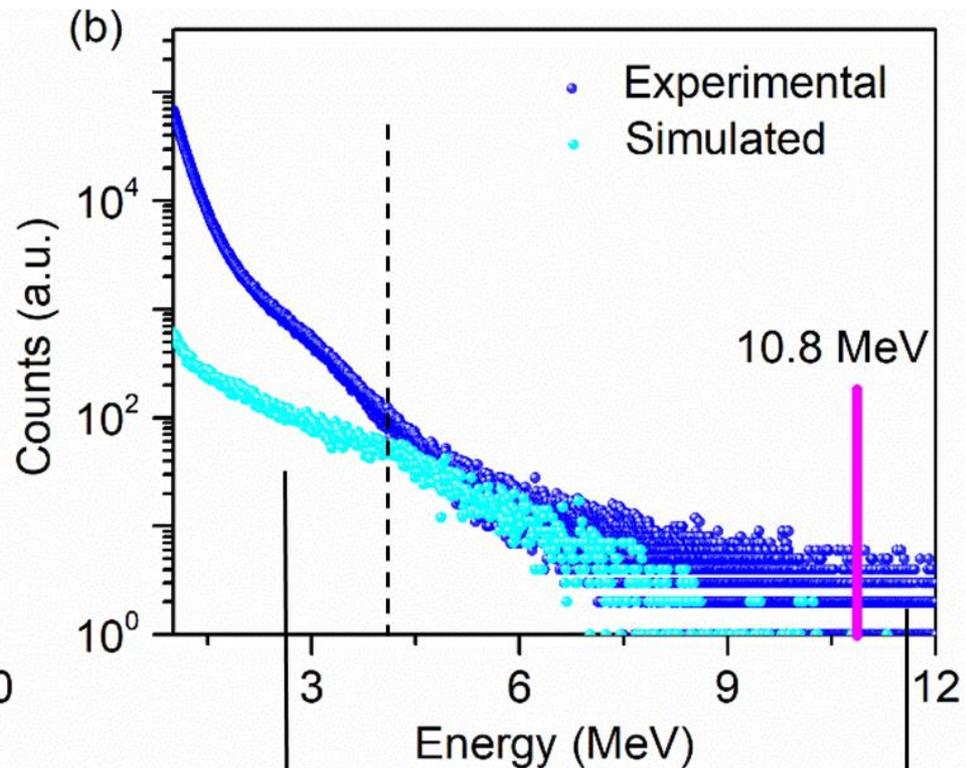
探测器电输运

2.3.1 基于4HCB有机半导体的直接型快中子探测

快中子能谱测试

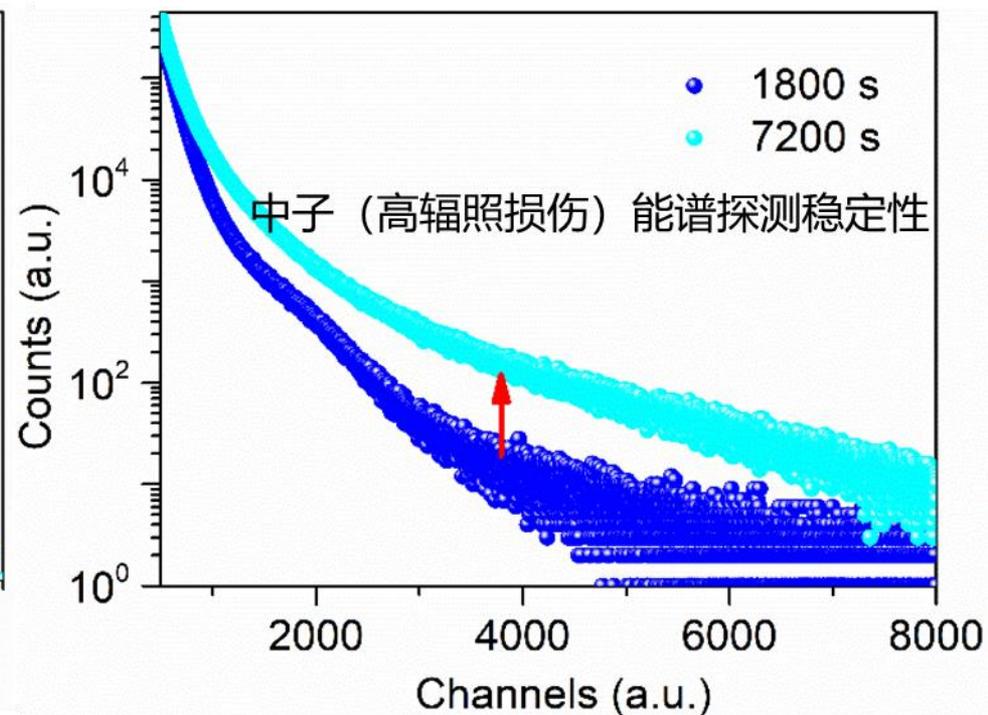
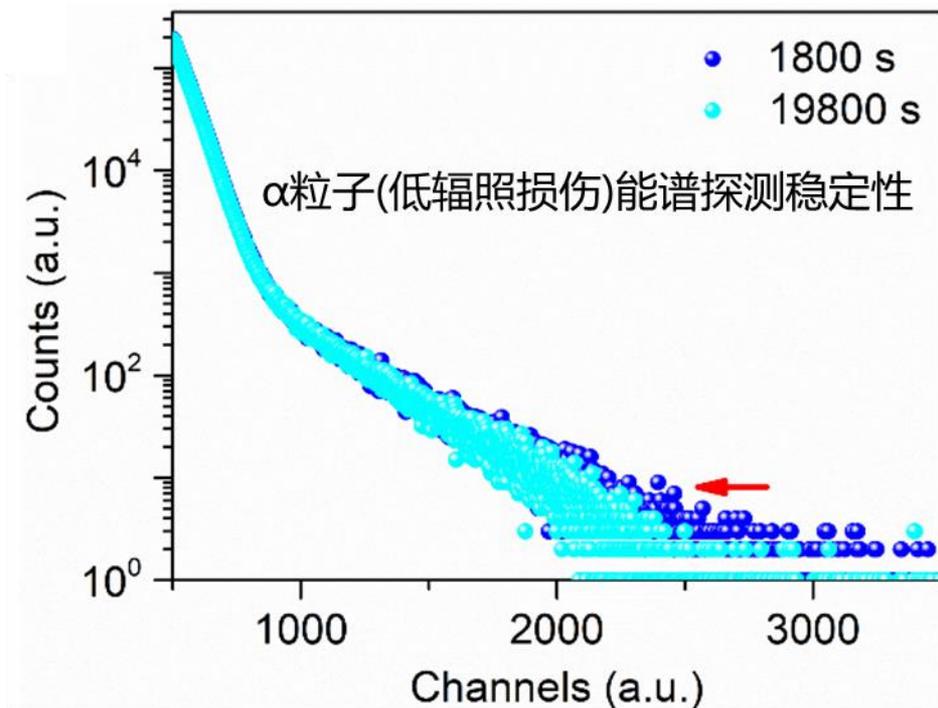


能谱采集时间: 30 min
探测效率: $15.8\% \text{ cm}^{-3}$



2.3.1 基于4HCB有机半导体的直接型快中子探测

4HCB探测器的能谱探测稳定性



- 噪声变高
- 能谱向高道指端漂移

2.1 基于4HCB有机半导体的直接型快中子探测

4HCB探测器的中子辐照损伤

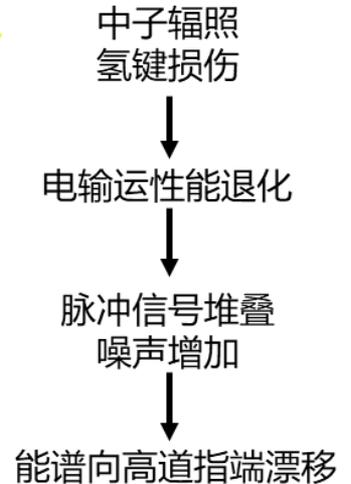
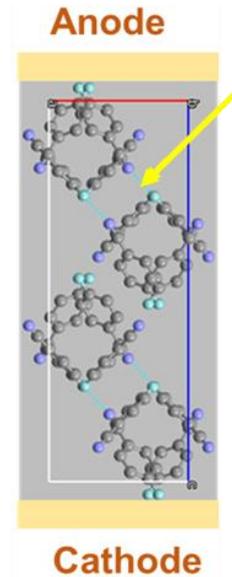
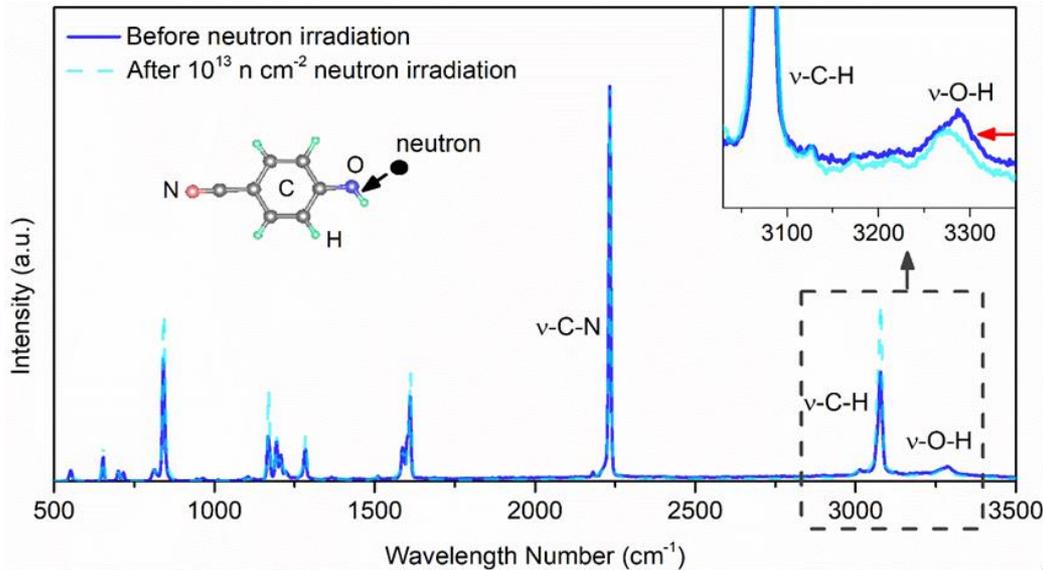
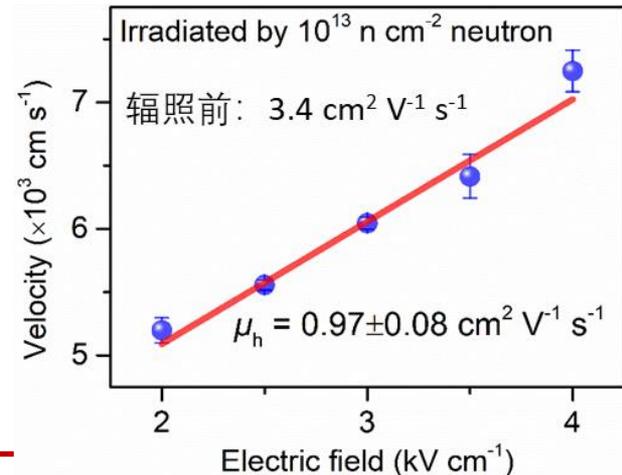


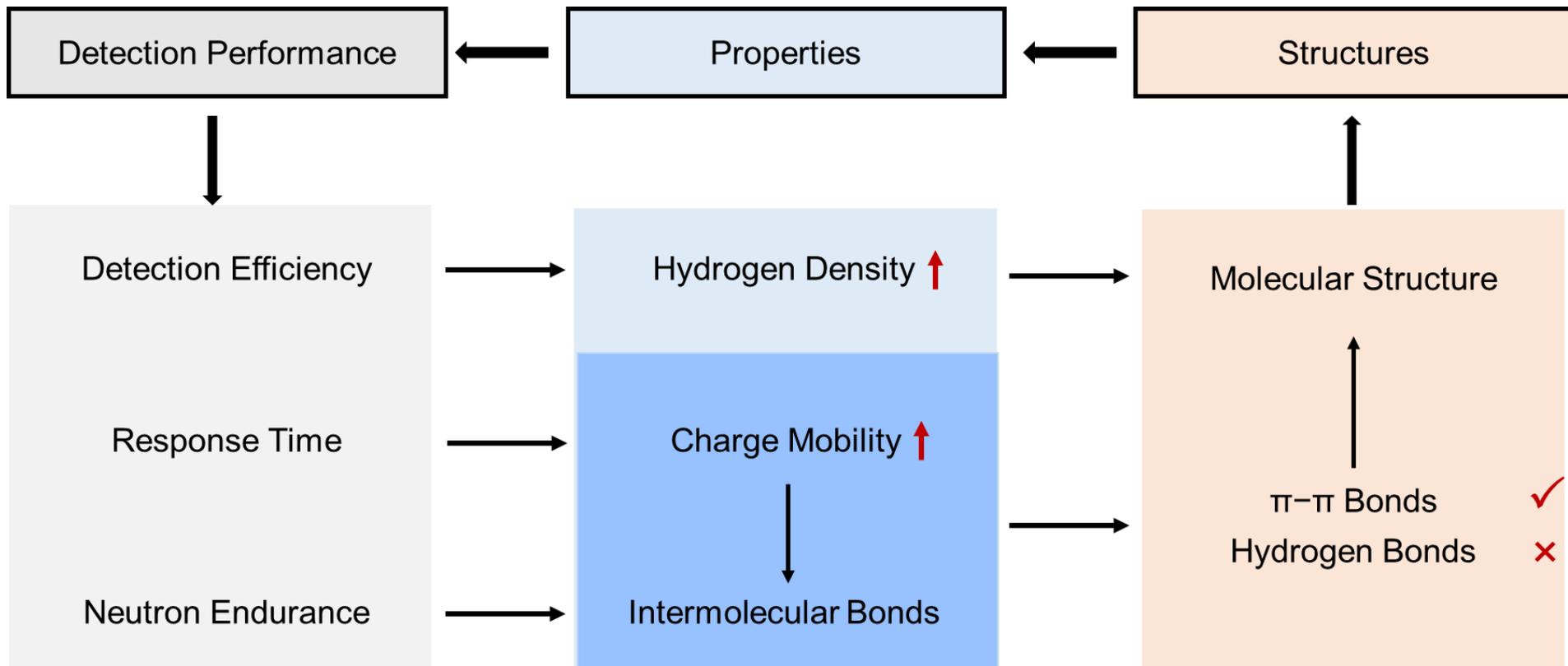
Table. Effects of Neutron irradiation on electrical properties

Neutron dose [⊖] (n·cm ⁻²) [⊖]	Peak center of [⊖] ν-OH (cm ⁻¹) [⊖]	Fermi energy level [⊖] (E _F -E _{HOMO}) (eV) [⊖]	Resistivity [⊖] (Ω·cm) [⊖]
0 [⊖]	3286 [⊖]	0.402±0.012 [⊖]	1.10±0.01×10 ¹² ⊖
10 ¹¹ [⊖]	3281 [⊖]	0.412±0.013 [⊖]	2.95±0.05×10 ¹² ⊖
10 ¹² [⊖]	3275 [⊖]	0.427±0.011 [⊖]	5.20±0.02×10 ¹² ⊖
10 ¹³ [⊖]	3272 [⊖]	0.456±0.012 [⊖]	1.08±0.07×10 ¹³ ⊖



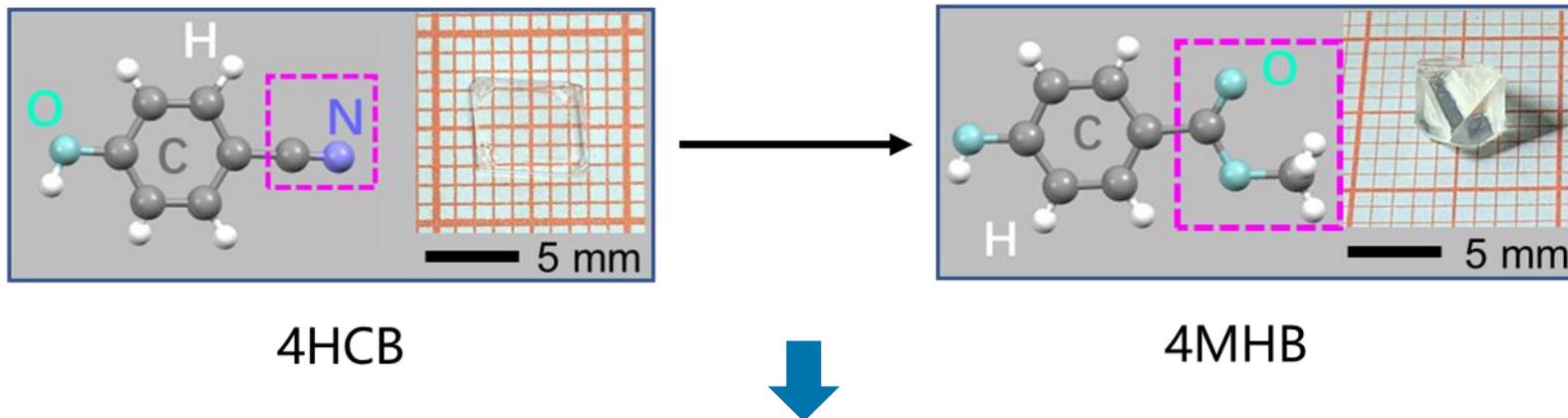
2.3.1 基于4HCB有机半导体的直接型快中子探测

半导体型快中子探测器材料优化思路



2.3.2 基于4HCB的分子裁剪优化中子探测性能

4HCB 分子结构裁剪



4HCB

4MHB

4MHB 及 4HCB 单晶有机半导体 H 核密度对比

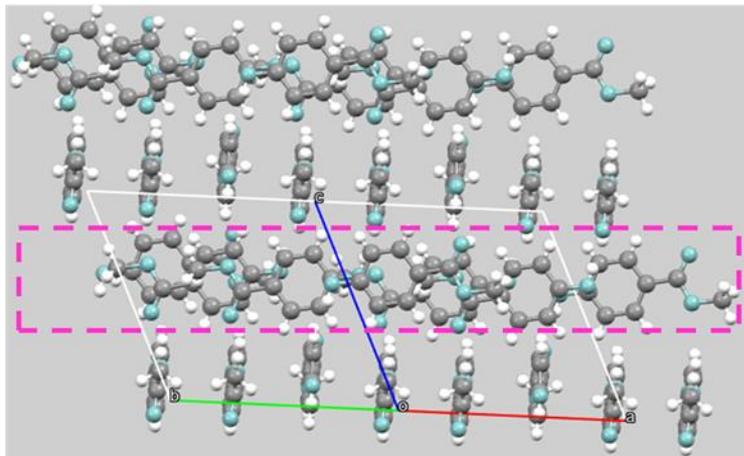
Materials	Chemical Formula	Density (g cm ⁻³)	Density of hydrogen atoms in functional groups (n cm ⁻³)	Density of hydrogen atoms in molecules (n cm ⁻³)
4HCB	X-CN	1.26	6.4×10^{21}	3.2×10^{22}
4MHB	X-COOCH ₃	1.46	2.0×10^{22}	4.2×10^{22}

X为-HO-C₆H₄

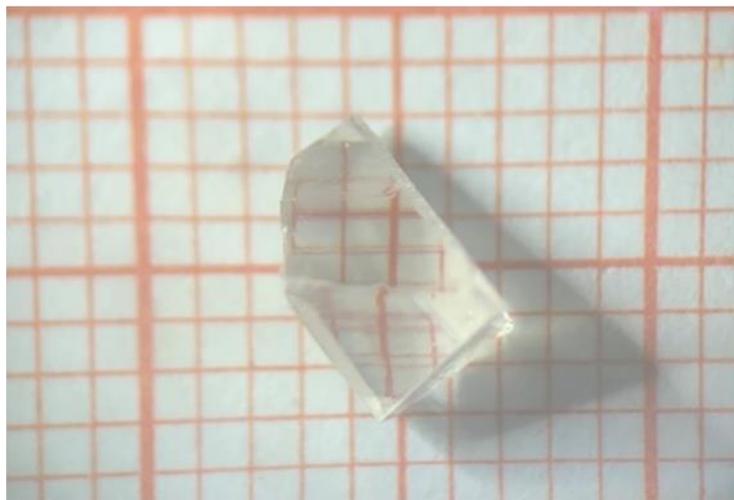
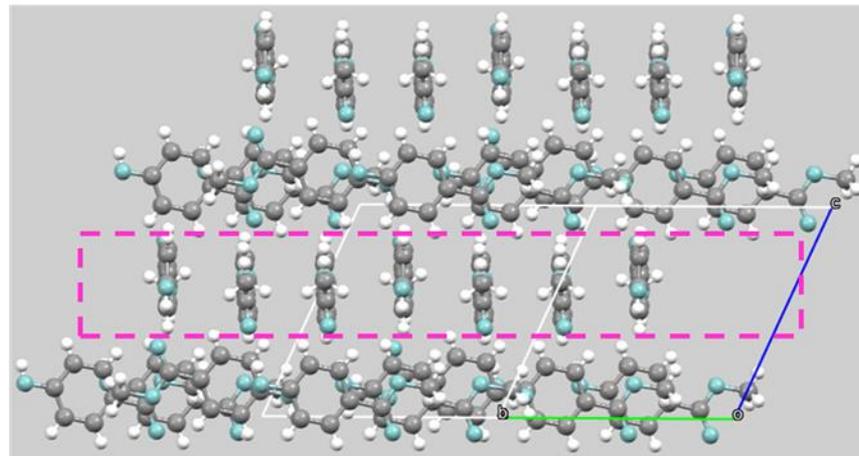
2.3.2 基于4HCB的分子裁剪优化中子探测性能

4MHB分子堆垛

View from [110]



View from [1-10]



π - π 键

三维
形貌

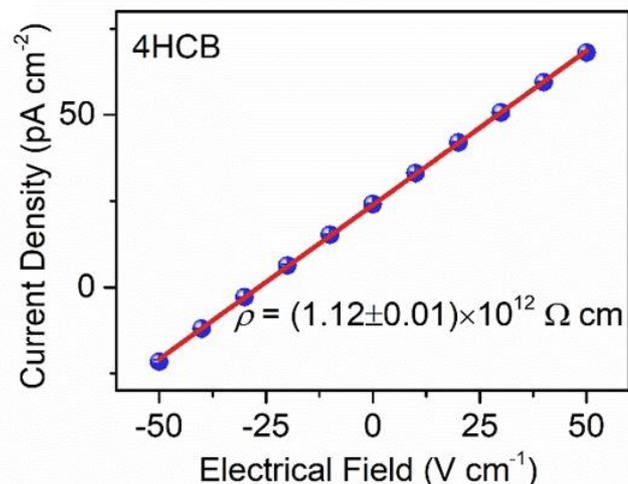
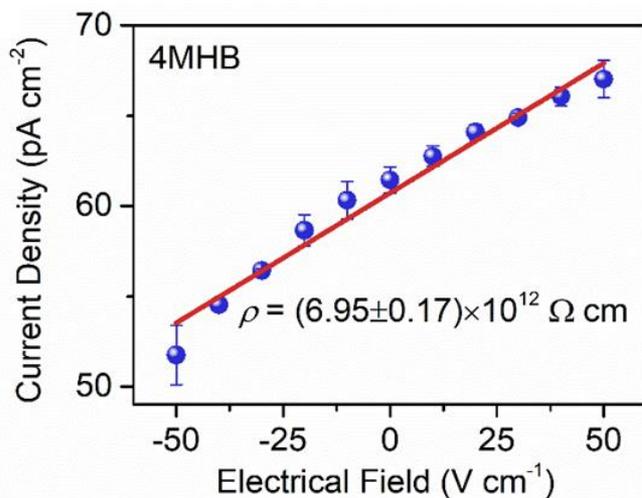
载流子运输
性能优异

耐辐照

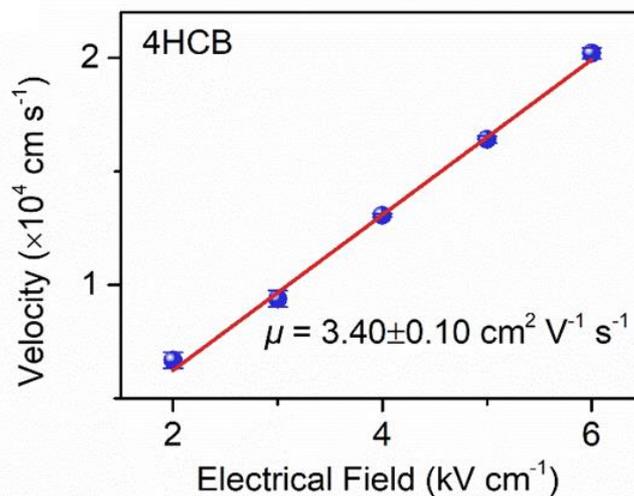
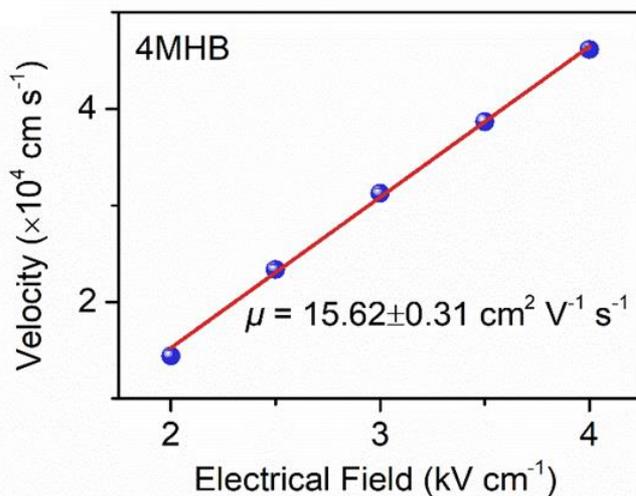
2.3.2 基于4HCB的分子裁剪优化中子探测性能

电学性能

电阻率



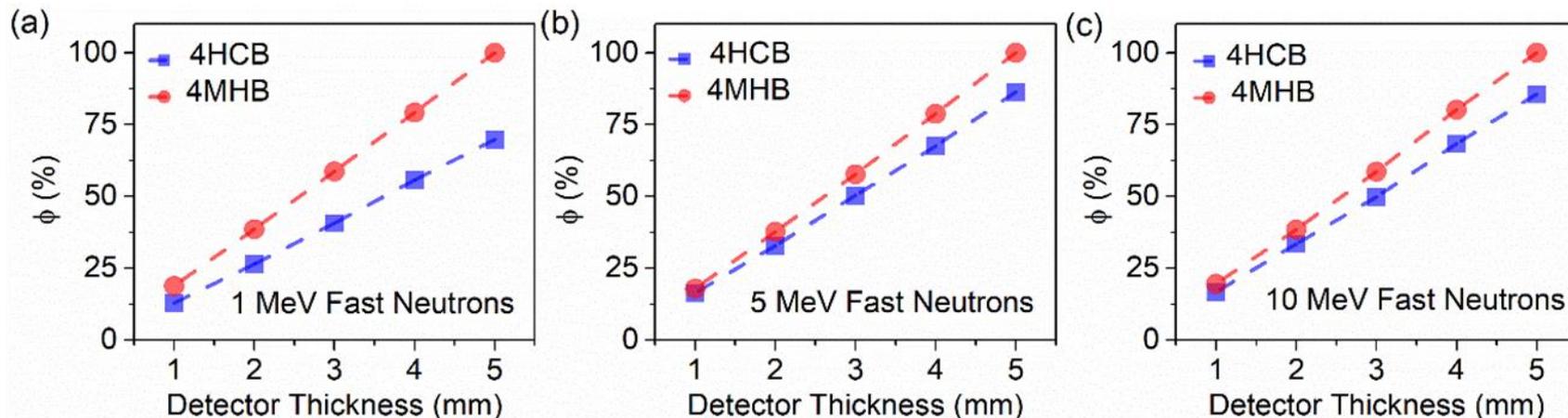
迁移率



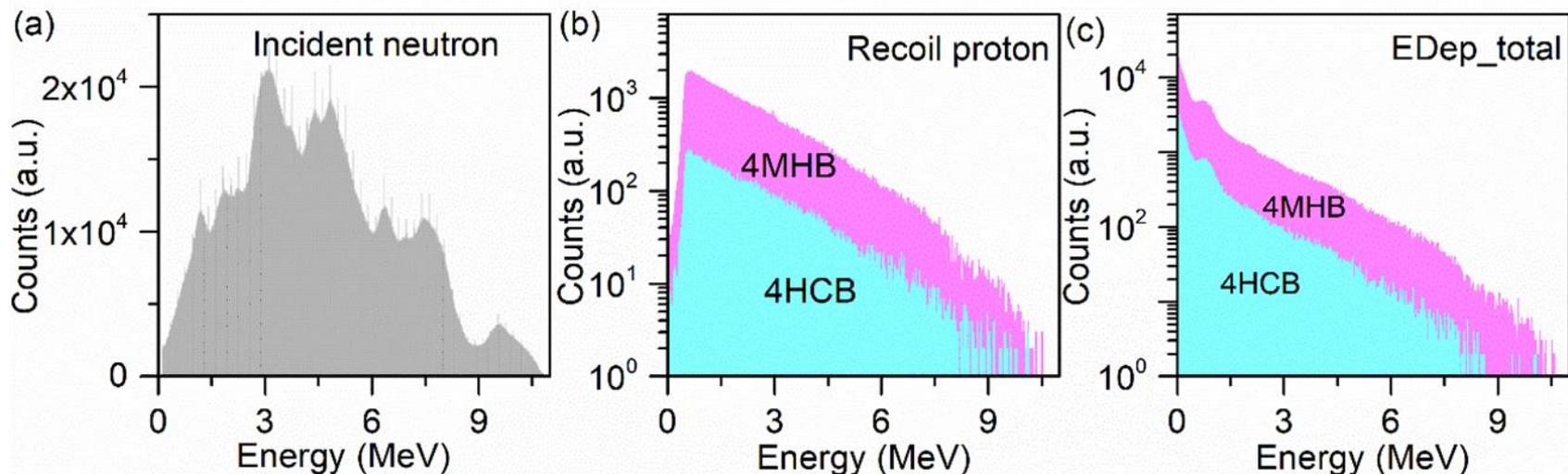
2.3.2 基于4HCB的分子裁剪优化中子探测性能

快中子吸收效率：蒙特卡罗模拟

中子吸收率

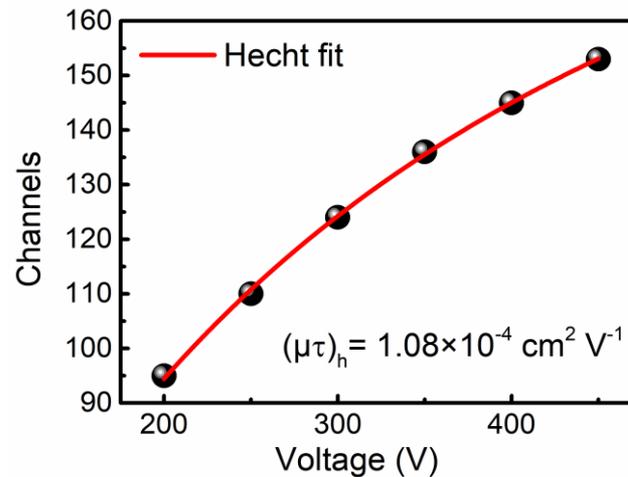
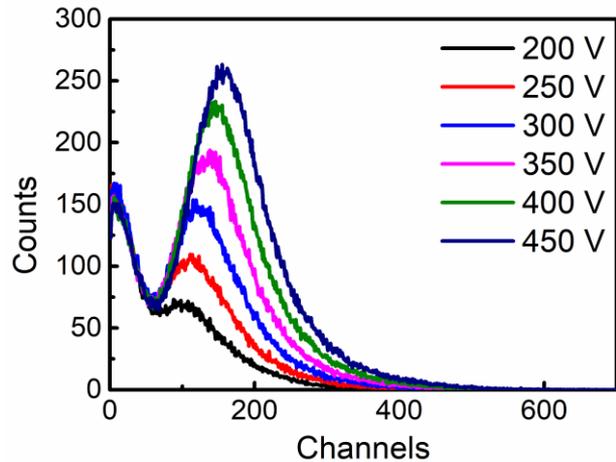
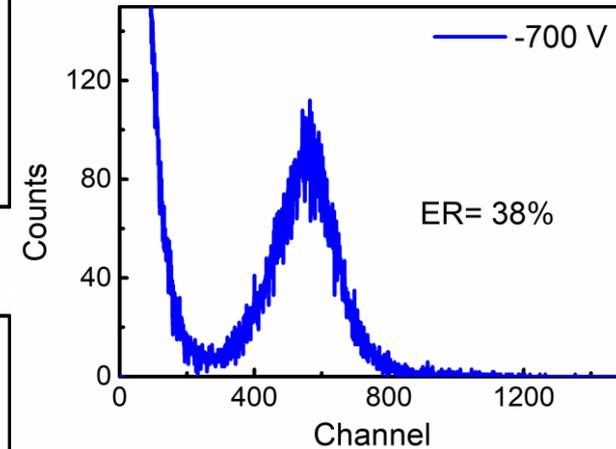
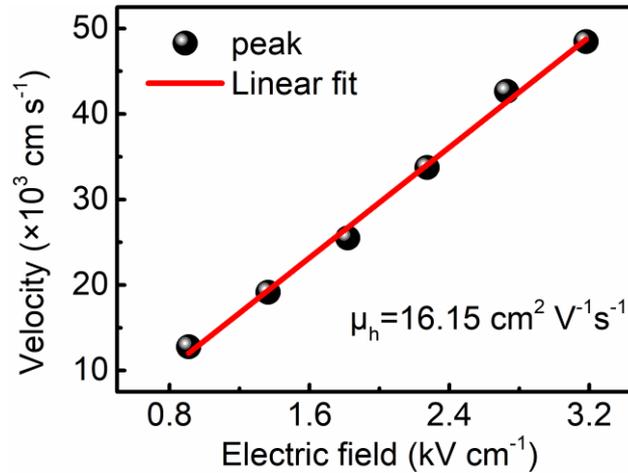
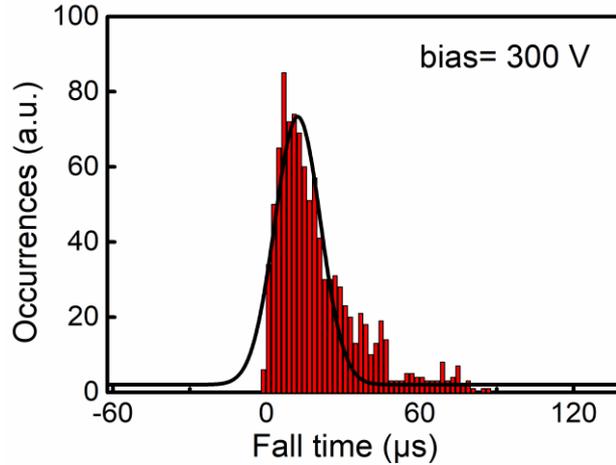


中子能量沉积谱



2.3.2 基于4HCB的分子裁剪优化中子探测性能

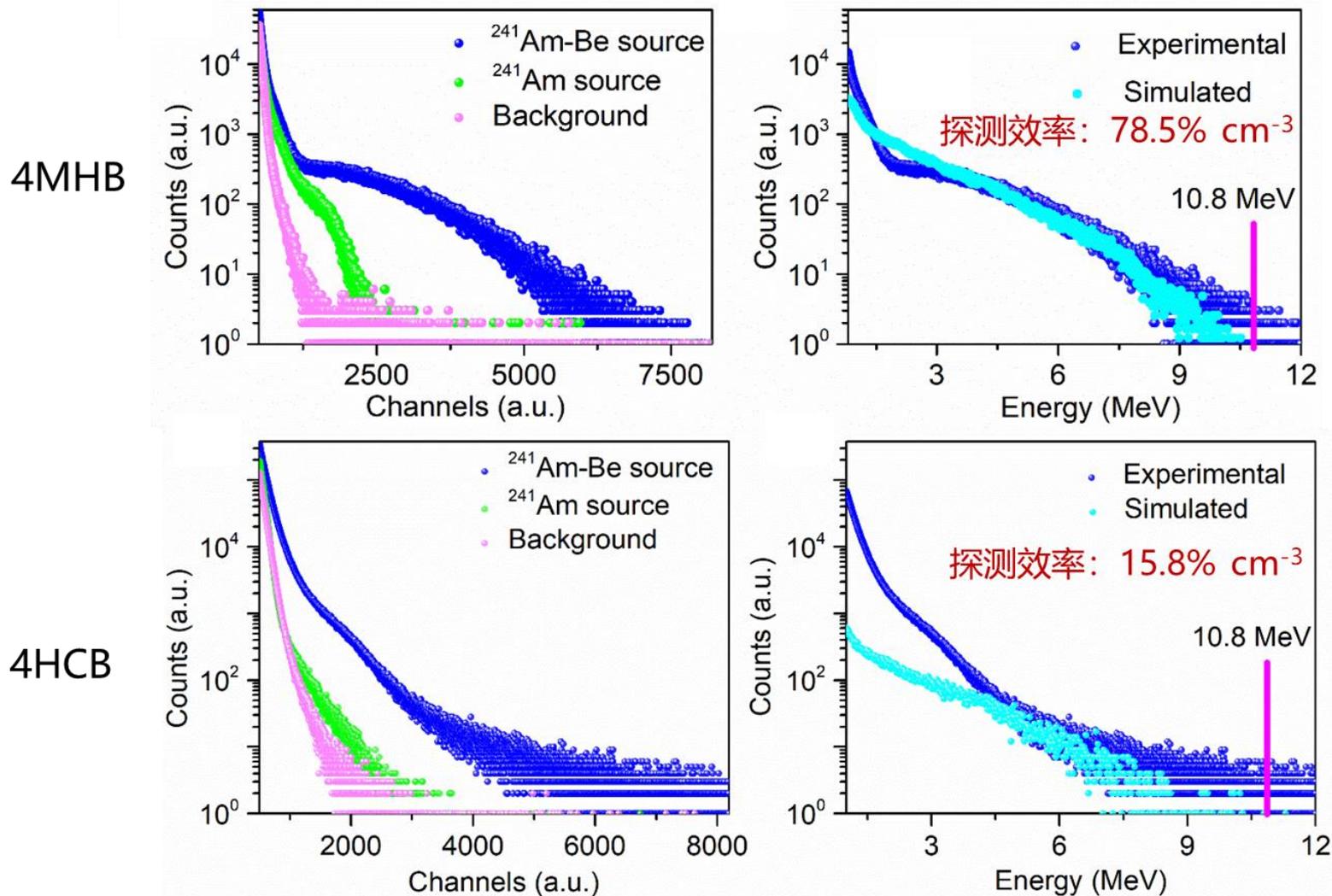
4MHB带电粒子探测能力：迁移率与能谱



全能峰分辨率38%

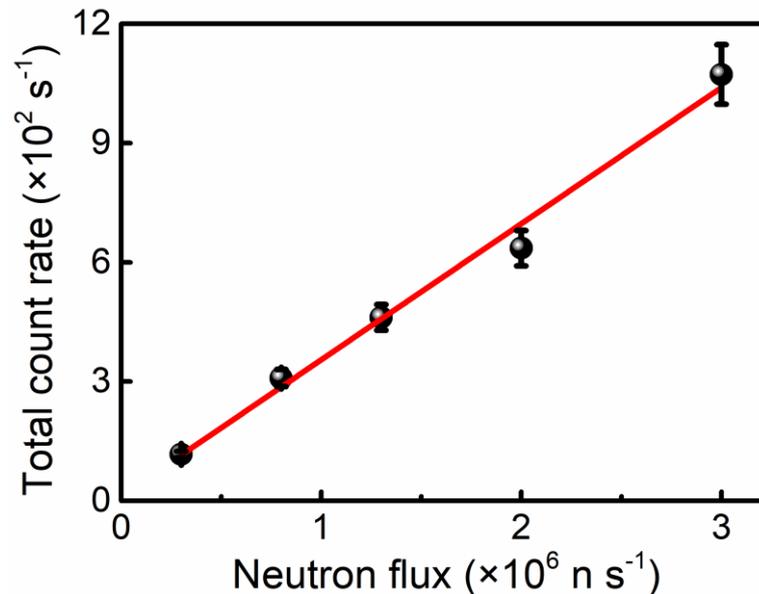
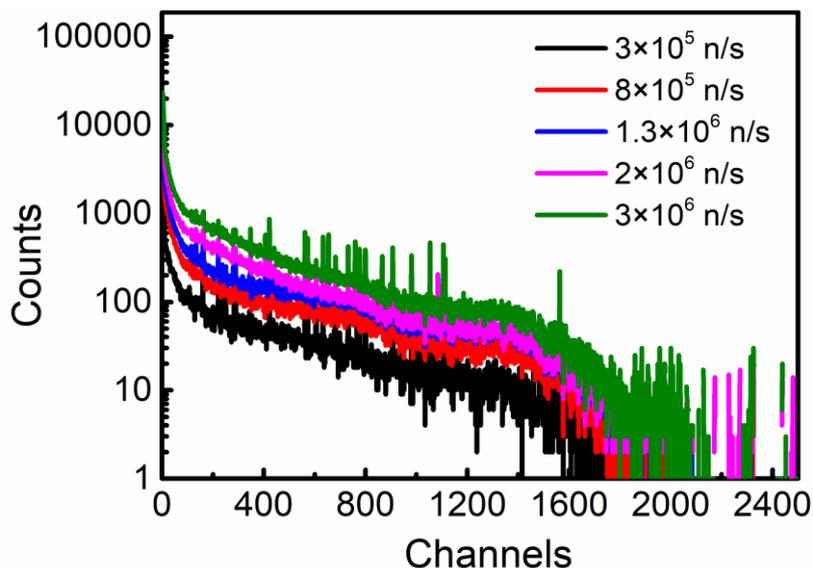
2.3.2 基于4HCB的分子裁剪优化中子探测性能

探测效率及能量分辨能力



2.3.2 基于4HCB的分子裁剪优化中子探测性能

D-D中子管能谱及线性响应



- 不同通量的单能中子能谱，为典型的反冲质子矩形谱；
- 总计数率与中子通量间展现了良好的线性响应；

目录

1. 研究背景

2. 研究内容

- CZT热中子探测器
- 基于 ${}^6\text{LiInSe}_2$ 晶体的热中子探测器
- 直接型快中子探测用全有机晶体

3. 结论与展望

3. 结论与展望

■ 围绕中子探测，开展晶体生长-缺陷调控-器件设计和制备研究

1. 制备出高能量分辨CdZnTe探测器，完成了热中子探测的试验验证
2. 针对热中子探测，实现直径30mm的 ${}^6\text{LiInSe}_2$ 晶体生长和器件制备
3. 通过分子改性等策略进行材料结构的设计及性能调控，获得满足快中子探测厘米级有机半导体单晶

请各位专家批评指正!