光散射的唯象描述及其布里渊散射和拉曼散射的应用与研究

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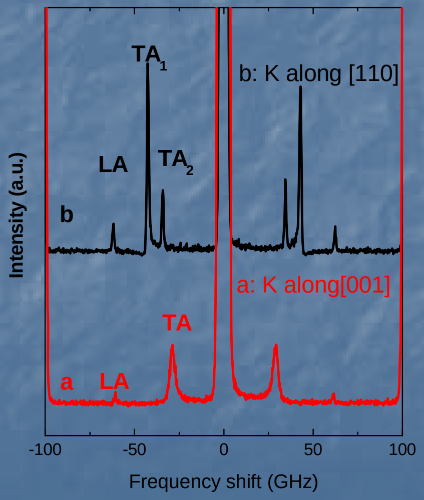
目 录

1899年；瑞利（Rayleigh)散射

处理了悬浮于介质中球形小颗粒所引起的光散射问题。得出散射光强度除与散射方向有关外，与激发波长λ^4成反比。白光中紫光的波长最短，所以它的散射光颜色带篮。这种散射叫做瑞利散射。其特点是散射光的频率不变。

1914－1922年；布里渊 Brillouin）散射

1914年布里渊开始对散射光的频谱进行了研究。1922年他计算了当散射体中存在声波引起密度涨落时散射光中的频率分布，发现在入射光频率（瑞利散射）的附近应该对称地分布着分离的谱线，这些谱线与入射光的频率差值，由声波的速度来决定。1930年Gross首先在液体中观察到了布里渊双线。这种光散射一般称为布里渊散射，它的频移很小。



Ce:BaTiO$_3$的布里渊散射光谱

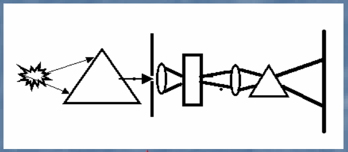
$$\omega_s = \omega_0 \pm \omega_q = \omega_0 \pm v_q k_q$$

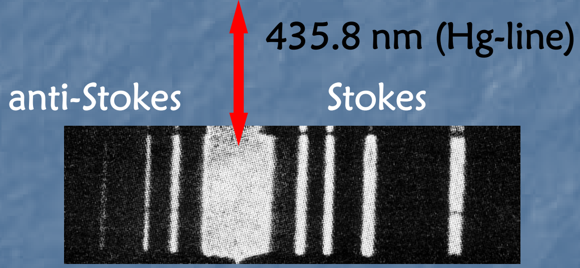
其中 $\omega_q = k v_q, k_q = \frac{4\pi n}{\lambda_0}\sin\frac{\theta}{2}$

光散射发展简述

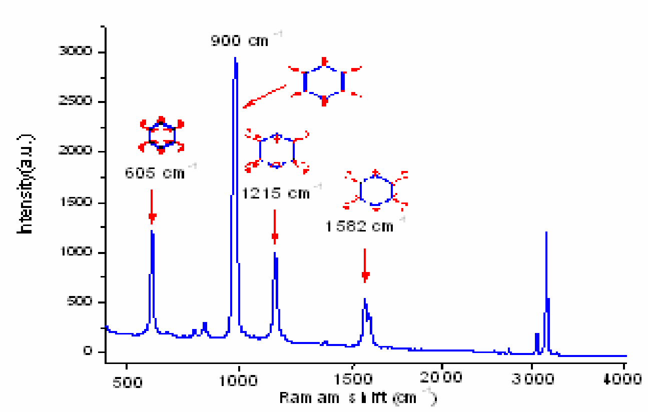
1930年诺贝尔物理学奖（拉曼（Raman）效应）

印度物理学家拉曼（Raman）从实验上观察到：单色的光照射到液体苯时，他发现在散射光中除了含与入射光相同频率的光外，还有更多与入射光频率发生位移（频移增加和减少）且强度极弱的谱线。前者就是已知的**瑞利散射**，后者是新发现的，是由分子振动所引起的散射。后来就以发现者拉曼的名字命名的拉曼散射光，称为拉曼散射效应。为此，拉曼获得1930年度的诺贝尔物理学奖。从拉曼光谱的研究，可以得到有关分子振动或转动的信息。



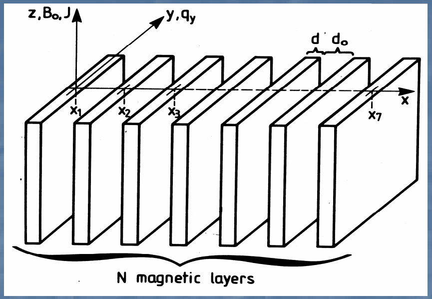


Resolution ca. 10 cm−1
Sample Volume: ca. 1 liter
Exposure time: ca. 40 hours

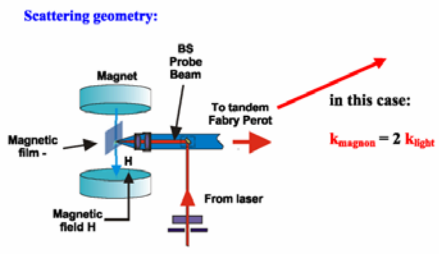


光散射发展史简述

2007年诺贝尔物理学奖－巨磁阻效应与布里渊散射



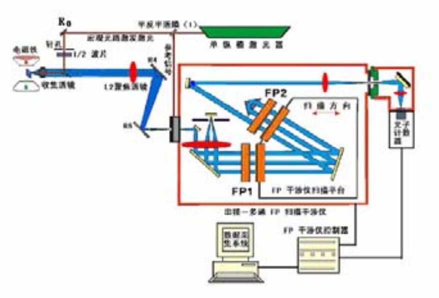
金属磁性多层膜



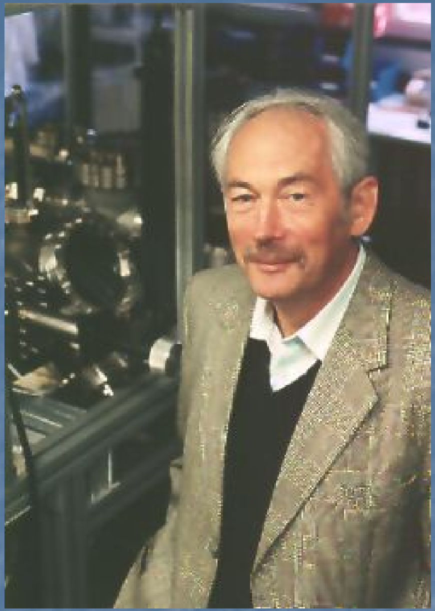
Scattering geometry:

in this case:

$k_{magnon} = 2\ k_{light}$

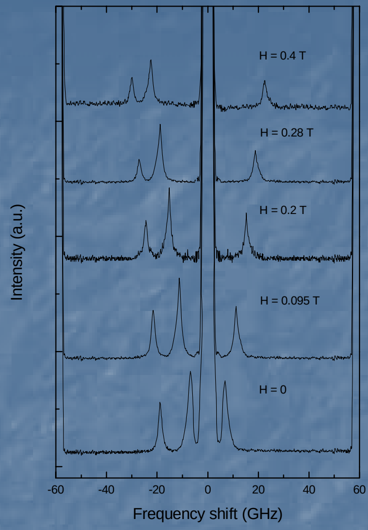


布里渊散射光谱仪原理图

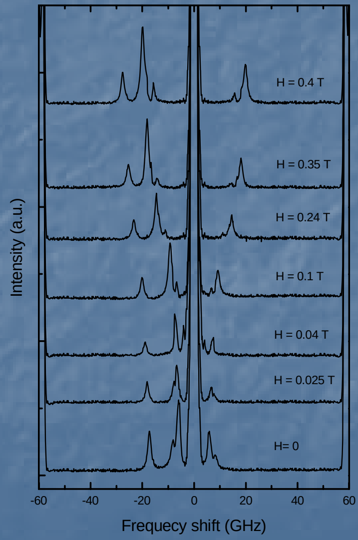


Prof. P. Grunberg

布里渊散射光谱仪



铁磁性耦合多层膜的布里渊散射光谱



反铁磁性耦合多层膜的布里渊散射光谱

光散射发展史简述

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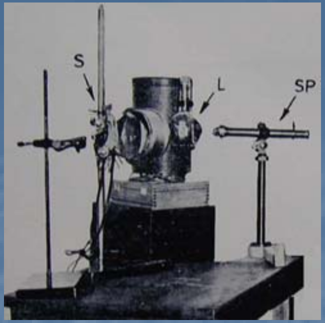
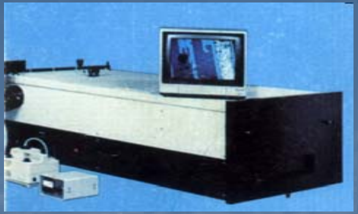
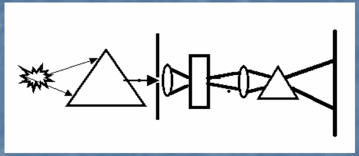
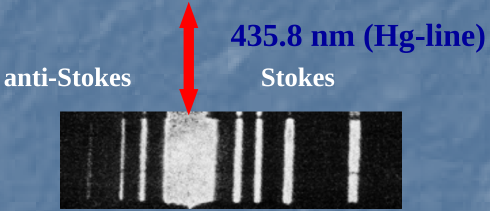


革命性发展 →

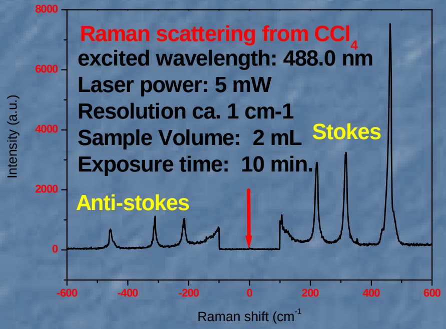


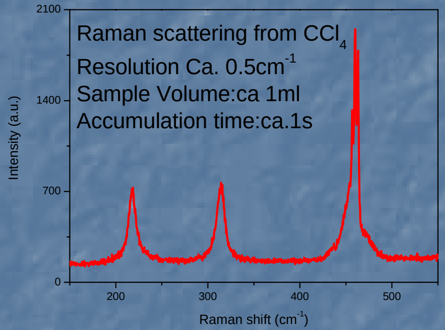
飞跃性发展 →

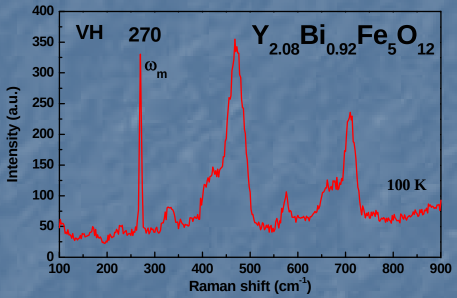


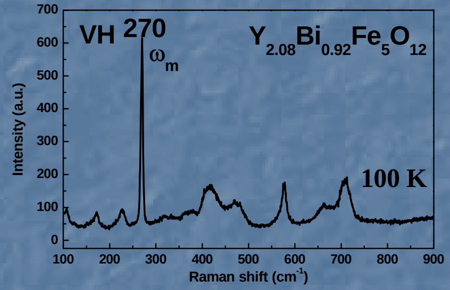


Resolution ca. 10 cm-1
Sample Volume: ca. 1 liter
Exposure time: ca. 40 hours





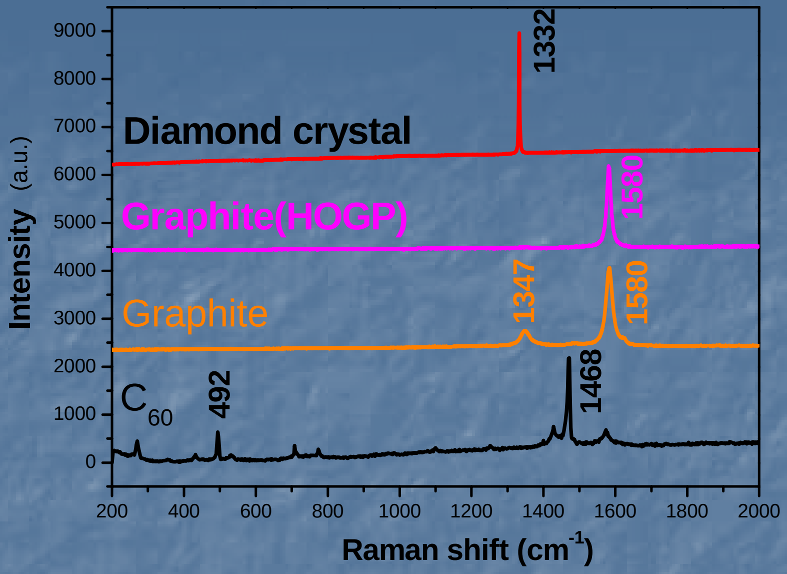


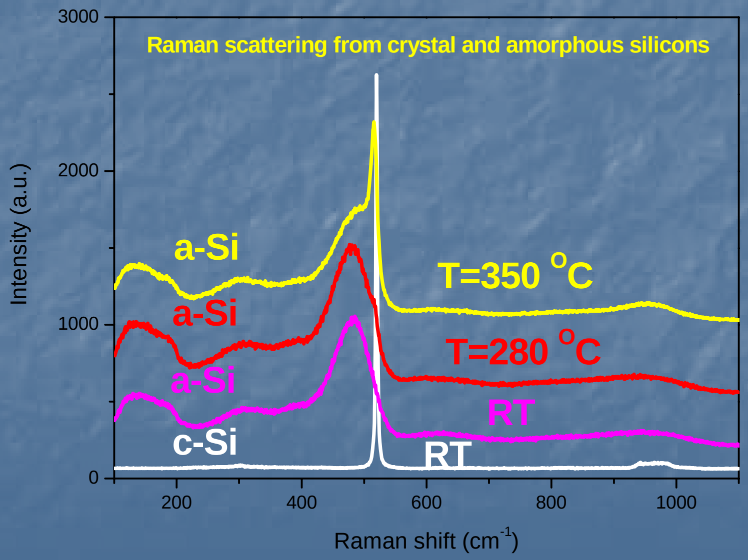


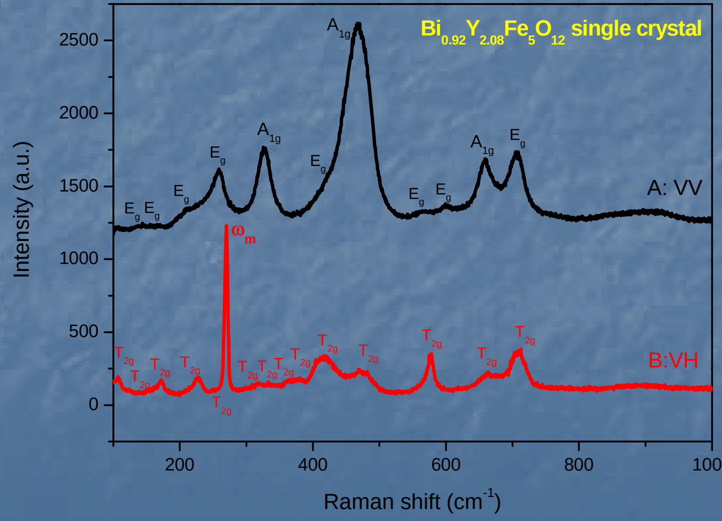
光散射研究经久不衰的原因：1、 激光技术的出现；激光的亮度高，单色性好、为光散射提供了优异的光源。2、单色仪、光学元件、光电探测器（PMT，CCD）和计算机等实验设备的精进。3、60年代后，分子光谱学，晶格动力学，固体物理的发展和元激发理论的兴起，群论方法提供了光谱分析的工具,为拉曼和布里渊散射研究既提供了理论背景，也提供了探索的对象。4、人为可控材料的不断诞生，也为光散射在分子和晶格振动光谱学方面的发展创造了条件，而且使之在其在物理，化学，材料，食品和生命与生化等研究领域上发挥日益重要的作用。

二、光散射的唯像描述与基本概念

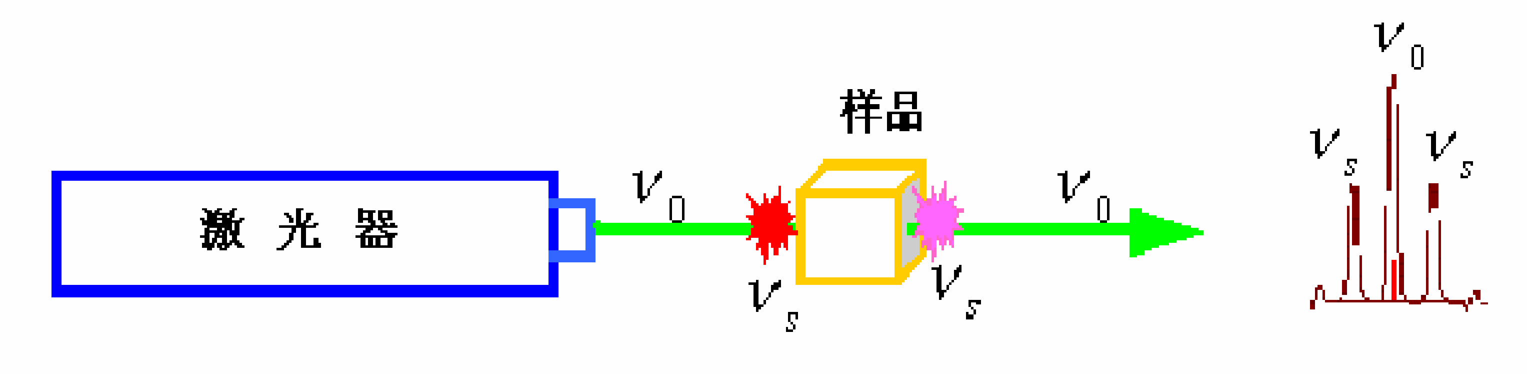
光散射包括原子的、分子的、晶体的以及一般固体的和凝聚态的材料，范围十分广泛。光散射是研究分子（固体）的振动或转动性质，固体元激发以及它们之间相互作用和物质鉴定的重要手段。通过对散射光谱中的频率，强度、线形以及偏振状态的分析，可以得到元激发和物种的信息。







二、光散射的唯像描述与基本概念

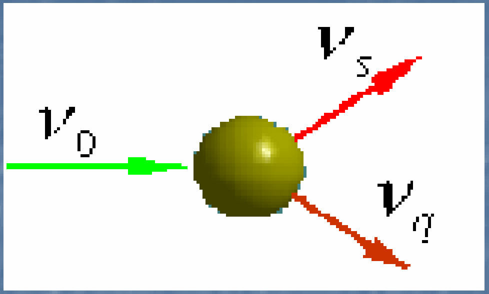


光在介质中的传播和散射

当频率为 ν_0 激光束射入介质后，除了被介质吸收的光之外，大部分仍以频率为的 ν_0 光沿入射方向穿过介质，还有一小部分光被介质散射到四面八方，并且改变了方向。散射光中不仅有频率为 ν_0 的入射光而且还包含有频率为的 ν_s 散射光。散射光的频谱如图所示。

二、光散射的唯像描述与基本概念

简单的光散射过程

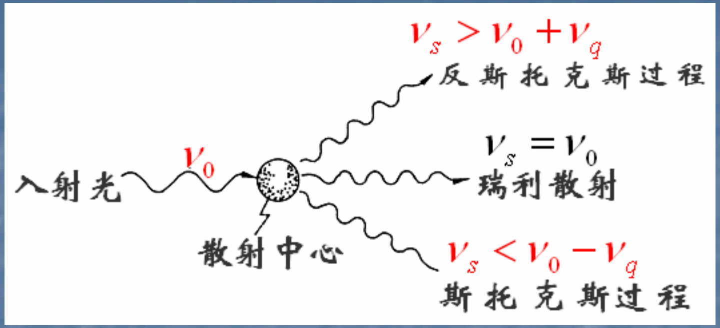


光子与元激发粒子碰撞示意图

为什么入射光与介质体系会发生能量的转移?

从粒子相互作用的角度最容易理解光的散射过程。光由光子组成，这是光的微粒性。照射到介质上的一束光，就是一束粒子－光子，每个光子有确定的能量 $h\nu_0$ ，动量 hk_0。光与介质的相互作用，就是光子和介质中的粒子（原子、离子、电子等）、准粒子（或称元激发，如声子、自旋波等）交换能量的过程。粒子的碰撞有弹性、非弹性碰撞两种，光的散射也有弹性和非弹性光散射。我们以介质中的粒子和光子的相互作用为例着重说明弹性、非弹性散射过程，同时引入一些重要的名词和概念。

简单的光散射过程



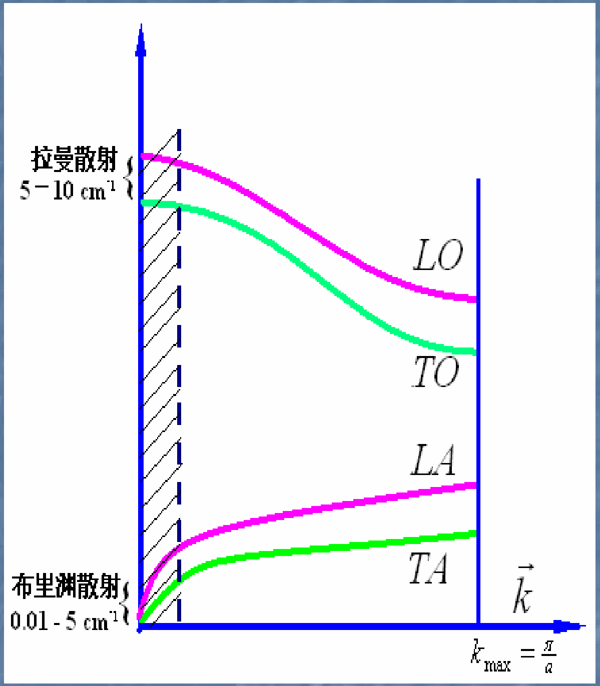
由于散射光的频率发生变化，说明入射光同物质发生发生了能量的转移。在光散射理论中；如$\nu_s = \nu_0$，入射光与物质没有能量的交换，称为Rayleigh散射。如 $\nu_s < \nu_0$,即一部分入射光能量交给了物质，光子失去能量，称为Stokes散射 。如 $\nu_s > \nu_0$，表明入射光从物质内部得到一部分能量，则称为反Stokes散射。

光散射的问题在于；什么原因造成这些频率的移动，换句话讲，为什么入射光与物质体系会发生能量的转移。只有把这个问题搞清楚，才能从散射实验中获得有用信息。

二、光散射的唯像描述与基本概念

非弹性光散射的种类：拉曼散射和布里渊散射

双原子链声子的色散关系为例：



非弹性光散射中：

- 光与光频支声子的能量交换，习惯上称为拉曼散射。其散射频移大约在10～5000 cm^{-1}范围。
- 光与声频支声子的能量交换，习惯上称为布里渊散射。其能量较小，散射频移大约0.01～2cm^{-1}范围。

非弹性光散射测量动量范围约为～10^5 cm^{-1}，非弹性中子散射的动量范围大至整个布里渊区(10^8 cm^{-1})。但它对样品需求量大，而且设备庞大和昂贵。

二、光散射的唯像描述与基本概念

拉曼和布里渊散射的基本研究内容

拉曼散射	布里渊散射
1. 分子的内部振动	1.分子的振动（外振动，转动）
2. 固体中的光频支声子	2.固体中的声频支声子
3. 光频支自旋波（交换自旋波）	3. 声频支自旋波（热激发的体自旋波，表面自旋波，铁磁/反铁磁多层膜中的层间偶尔交换自旋波）
4. 局域能级（朗道，施主，受主和晶场能级）	
5. 极化声子	
6.等离激元与声子的偶合	

(3.1) 非弹性光散射中的能量守恒和动量守恒

非弹性散射的经典理论：

由于光具有波动和粒子性质，也可以从光的波动性来分析非弹性散射光的产生。 照射在分子上的一束单色光（激光）的电场强度可以写成：

$$E = E_0 \cos \omega_0 t \qquad (3\text{-}1)$$

其中E_0是电磁场的振幅，ω_0是这束激光的频率。假如一个双原子分子在这激光的电场作用下，产生的感生电偶极矩（P），分子极化率以及电场强度的近似关系式为；

$$P = \alpha E = \alpha E_0 \cos \omega_0 t \qquad (3\text{-}2)$$

α 是分子的极化率。如果分子是在以振动频率为做简谐振动的话，原子核的位移量就可以写成:

$$q = q_0 \cos \omega_q t \qquad (3\text{-}3)$$

q_0是振动的振幅。对于一个小的振动振幅来讲，极化率可以是原子核位移量的线性函数，则可以按泰勒级数展开；

$$\alpha = \alpha_0 + (\frac{\partial \alpha}{\partial q})_0 q_0 + \ldots.. \qquad (3\text{-}4)$$

α_0 分子在平衡位置时的极化率，是相对于在平衡位置时，位移量发生改变时的极化率的变化率。将（3-3）和（3-4）式代入（3-2）式后，我们获得：

$$\begin{aligned} P &= \alpha E_0 \cos\omega_0 t \\ &= \alpha E_0 \cos\omega_0 t + (\frac{\partial \alpha}{\partial q})_0 q E_0 \cos\omega_0 t \\ &= \alpha E_0 \cos\omega_0 t + (\frac{\partial \alpha}{\partial q})_0 q E_0 \cos\omega_0 t \cos\omega_q t \qquad (3\text{-}5) \\ &= \alpha E_0 \cos 2\pi\nu_0 t + \frac{1}{2}(\frac{\partial \alpha}{\partial q})_0 q E_0 [\cos 2\pi(\nu_0 + \nu_q)t + \cos 2\pi(\nu_0 - \nu_q)t] \end{aligned}$$

由经典电磁理论可知，从(3-5) 式中可以看出，线性感生偶极矩具有3个不同频率分量：1：是散射光的频率与入射光的频率相同的是**瑞利散射**；2： 是散射光的频率为(ν_0+ ν_q)是**反斯托克斯的散射**；3：是散射光的频率为（ ν_0- ν_q ）是**斯托克斯散射。**从（3-5）式可以看出，散射光与入射光的差值即分子（或其它元激发）的振动波数，这就是非弹性散射。

三、非弹性散射的基本特点

(3-5) 式中若：

$$\nu_s = \nu_0 - \nu_q \qquad \text{或者} \qquad \Delta\nu = \nu_0 - \nu_q$$

$$\vec{k}_s = \vec{k}_0 - \vec{k}_q \qquad\qquad \Delta\vec{k} = \vec{k}_0 - \vec{k}_q \qquad \text{（3−6）}$$

即为Stokes散射

若**(3-5)**式为：

$$\nu_s = \nu_0 + \nu_q \qquad \text{或者} \qquad \Delta\nu = \nu_0 - \nu_q \qquad \text{（3−7）}$$

$$\vec{k}_s = \vec{k}_0 + \vec{k}_q \qquad\qquad \Delta\vec{k} = \vec{k}_0 - \vec{k}_q$$

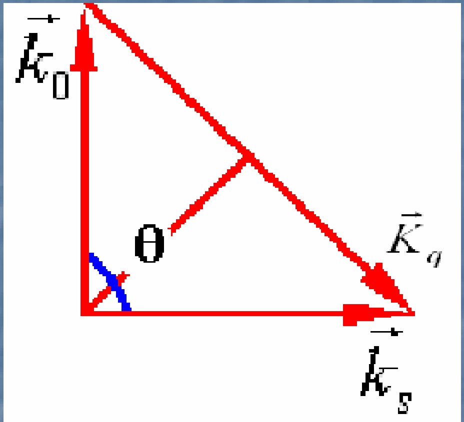
即为反Stokes过程。

（**3-6**）和（**3-7**）式 分别代表正反Stokes散射的能量守恒和动量守恒。

3.2、非弹性光散射的散射波矢与散射配置

由一阶散射过程的动量守恒关系可知，入射光，散射光和介质内元激发的波矢之间的关系可用三角形表示。散射中光频移相对光频本身是很小的，即 $|\vec{K}_s| \approx |\vec{K}_0|$ ，波矢三角形近似为等腰三角形。这样元激发波矢和光波之间有；

$$|k_q| = 2\cdot|k_0|\cdot n\cdot\sin\frac{\theta}{2} \qquad (3\text{-}8)$$



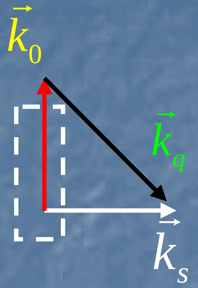
入射、散射光和介质内元激发的波矢之间的关系

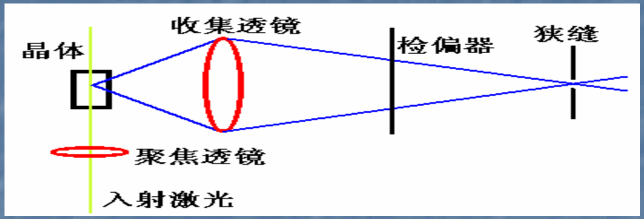
式中 n 是散射介质的折射率，θ 是入射、散射波矢之间的夹角。

三、非弹性散射的基本特点

非弹性光散射的散射波矢与散射配置

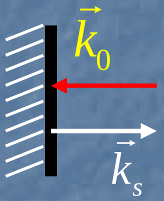
散射配置的标记：　$k_0(e_i^s e_j^0)k_s$

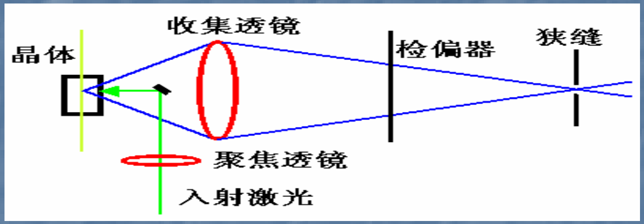




直角散射（90°散射）配置

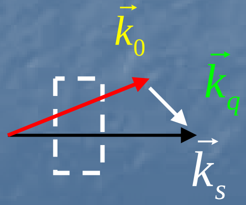
$x(zz)y; x(zx)y; x(xx)y; x(yx)y$

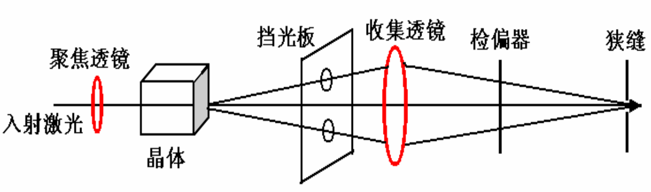




背向散射（180°散射）配置

$x(zz)\bar{x}; x(zy)\bar{x}; x(yy)\bar{x}$





前向散射（0°散射）配置

$y(zz)y; y(zx)y; y(xx)y$

三、非弹性散射的基本特点

3.3、能量守恒和动量守恒的应用：

拉曼散射的甄别

a：只要是拉曼散射就会有斯托克斯线和反斯托克斯线同时对称出现

斯托克斯散射：$\nu_s < \nu_0$

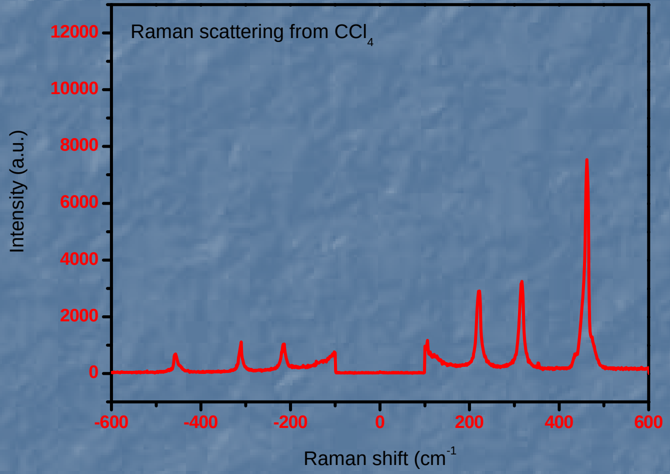
$$\nu_s = \nu_0 - \nu_q$$

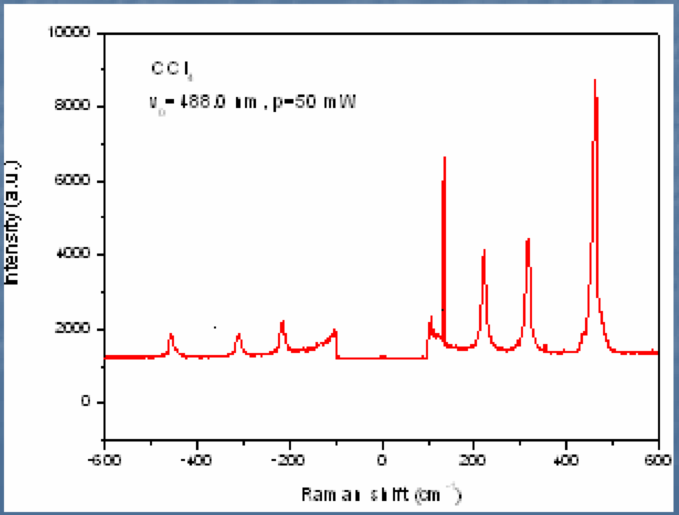
$$\vec{k}_s = \vec{k}_0 - \vec{k}_q$$

反斯托克斯散射：$\nu_s > \nu_0$

$$\nu_s = \nu_0 + \nu_q$$

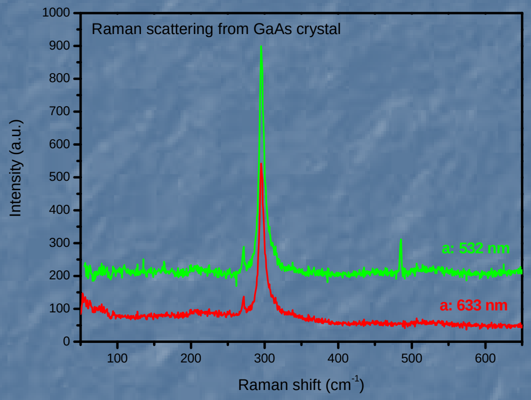
$$\vec{k}_s = \vec{k}_0 + \vec{k}_q$$



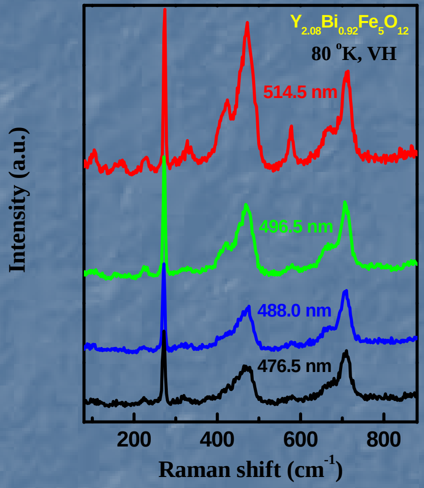


三、非弹性散射的基本特点

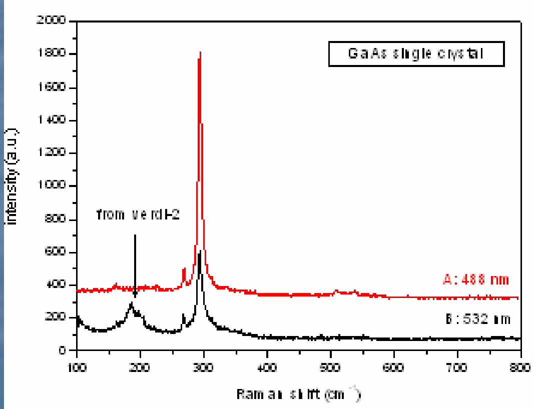
b. 对同一样品，它的拉曼频移只与分子（或声子）振动（转动）能级有关，与入射光的波长无关。



不同激发波长下的GaAs的拉曼散射光谱

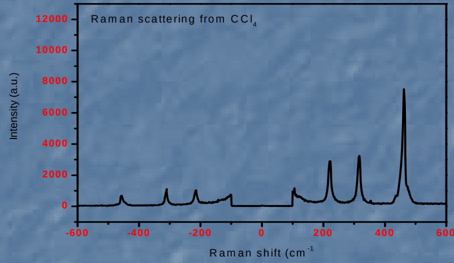


不同激发波长下的Bi-YIG的声子和磁子的拉曼散射光谱



三、非弹性散射的基本特点

c. 一般情况下，**斯托克斯线的散射强度比反斯托克斯线的散射强度大，**这是处于振动基态上的粒子数远大于处于振动激发态上的粒子数。散射强度遵循Boltzmann分布。

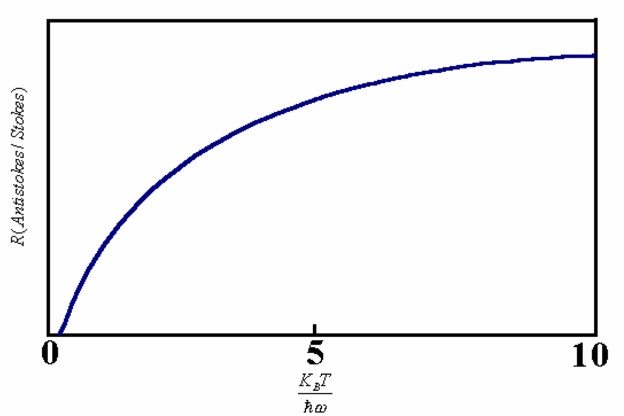


从正、反Stokes散射强度应彼此不同，其散射截面之比为：

$$R = \frac{d\sigma}{d\Omega}\bigg|_{A_s} \bigg/ \frac{d\sigma}{d\Omega}\bigg|_{S} = \frac{n(\omega)}{n(\omega)+1} = \frac{1}{e^{h\nu/kT}}$$

$$n(\omega) = \frac{1}{\exp\frac{h\nu}{k_B T} - 1}$$

拉曼散射实验中，在测量正、反Stokes散射峰的同时，也可以得到它们的积分强度，也就得到了R值。该公式可求出样品的表面温度。但它的重要性不仅在于可知样品的表面温度，而是可用它来判明散射的性质，是一级还是二级拉曼散射。



三、非弹性散射的基本特点

样品表面温度的测定（以CCl_4为例）

在入射激光功率为100 mW时，测得CCl_4在频移为460 cm^{-1}处的正反Stokes散射强度为2063522 counts 和250368 counts。

$$R=\left.\frac{d\sigma}{d\Omega}\right|_{A_s}\Big/\left.\frac{d\sigma}{d\Omega}\right|_{S}=\frac{n(\omega)}{n(\omega)+1}=\frac{1}{e^{h\nu/kT}}$$

$$T=-\frac{h\nu}{k_B\ln(I_{AS}/I_s)}$$

$$=-\{(6.63x10^{-34}x4.6x10^{2}x30x10^{9})/[1.38x10^{-23}x(-2.11)]\}$$

$$=914.94/2.91$$

$$=314.4(K)$$

$$h=6.63x10^{-34}JS;k_B=1.38x10^{-23}J/K$$

3.4、 动量守恒及其影响它的因素

拉曼光谱的谱形的宽化和非对称性的起因

如晶体中存在位错等其他缺陷，声子波在其中的传播是衰减的，即声子的特殊相关长度有限，导致动量守恒定则的松驰，即有一部分$k \neq 0$的声子也被激发。在拉曼光谱中，则表现为谱形的非对称化和宽化，同时会引起声子谱的红移。

$$I(\omega) \propto \int_0^1 \exp\left(-\frac{k^2L^2}{4}\right)\frac{dk^2}{[\omega-\omega(k)]^2+[\Gamma_0/2]} \qquad （3\text{-}9）$$

在这里为 ω 声子的频率；k 为声子的波氏；L为相关长度，它的大小直接反应晶体中缺陷密度的高低，L 值大，则缺陷密度低；Γ_0 为完整晶体的拉曼谱半峰宽。

考虑到布里渊区中心附近声子色散关系

$$\omega(k) = A + B\cos(\pi k) \qquad （3\text{-}10）$$

利用方程 (3-9) 和 (3-10) 能计算出拉曼峰的红移，相关长度L与半峰宽 Γ 的关系。

在不同温度下单晶Si的拉曼散射光谱

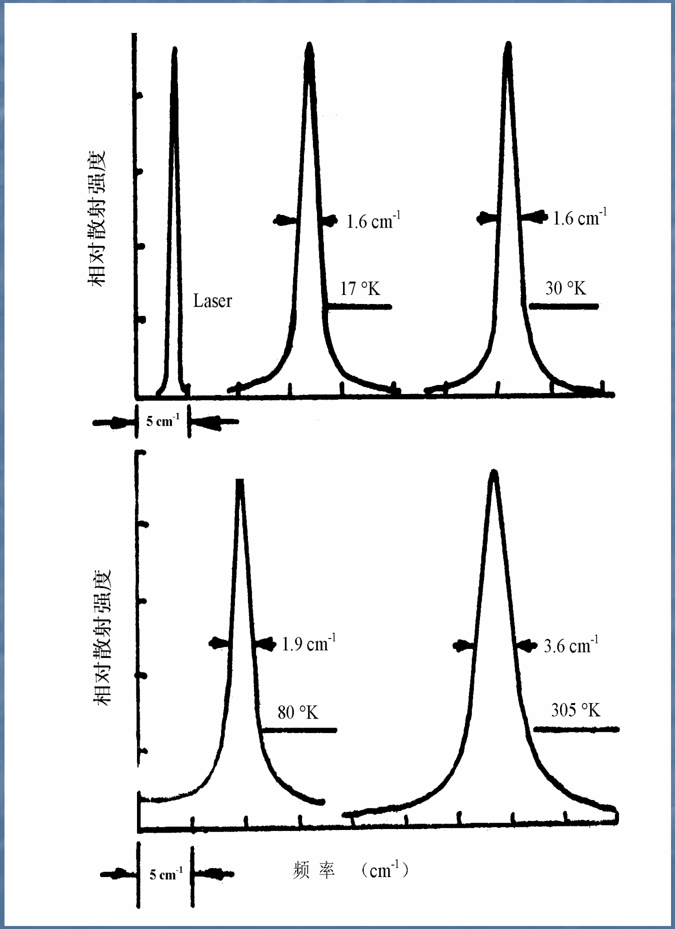
在不同温度下测得的单晶Si的拉曼光谱，其主要特征为；

1、散射峰为 Lorentz 线型。

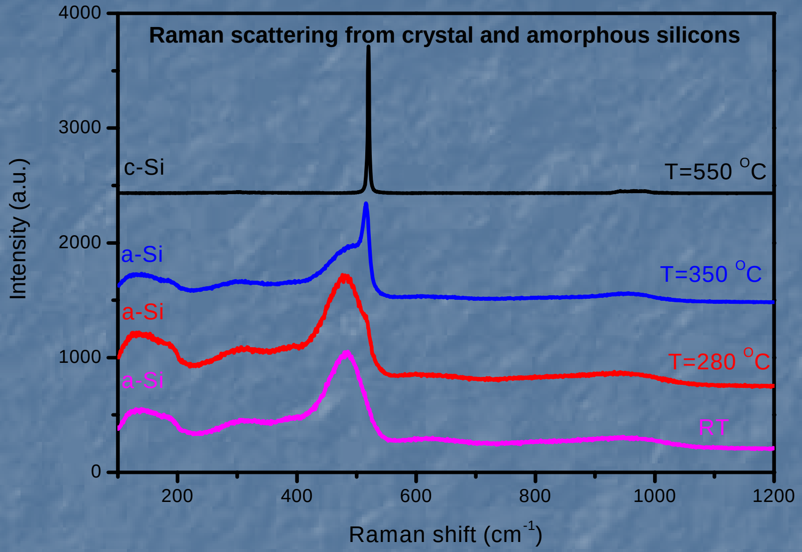
2、温度上升，线宽加大。

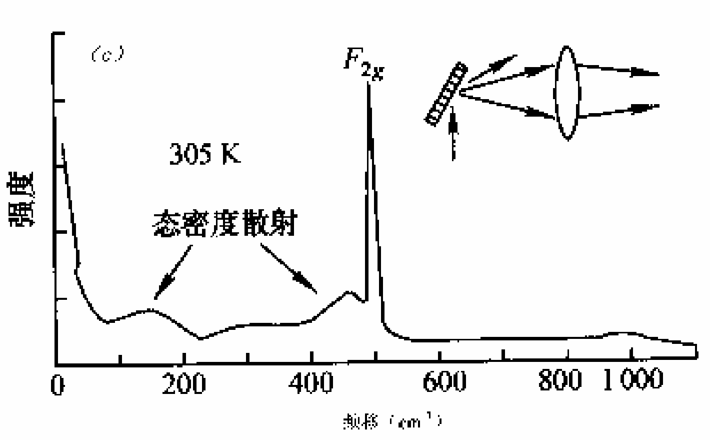
3、线宽$\Gamma = 1/\tau$, 故可以算出声子寿命。

4、温度升高，意味着样品中的声子寿命变短。



从非晶Si的拉曼散射的变化看动量守恒演变





非晶态的Si与单晶Si的光谱相比，差别在于：

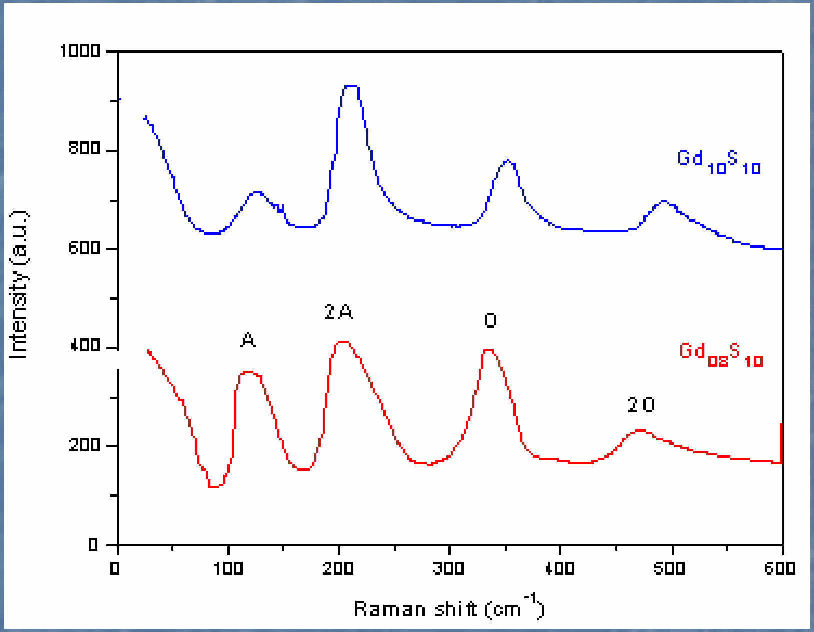
1、散射峰极大值偏离单晶Si所在的位置，由于长程无序破坏了动量守恒，散射光谱中没有了简并的TO，LO声子散射峰，实际上这个拉曼光谱反映了Si的单声子态密度。

2、除520 cm^{-1} 附近的峰以外，100－200 cm^{-1}区域也出现了散射峰，理论分析：它于声频支声子的态密度有关。

三、非弹性散射的基本特点

周期性晶格中有缺陷所感应的拉曼散射

改变GdS样品中的成份配比，得到以下光谱图。比较这二个样品的的光谱发现，猜想的来自一阶拉曼散射的振动峰都随成份的改变而增强了。这是因为在组分比为1：0.8的 GdS 样品内，由于原子的失配，晶体的周期性遭到破坏，即缺陷增多缺陷感应，拉曼散射也增强了。而二阶拉曼散射并不随缺陷的增多而增强。



GdS 成份配比的拉曼散射光谱

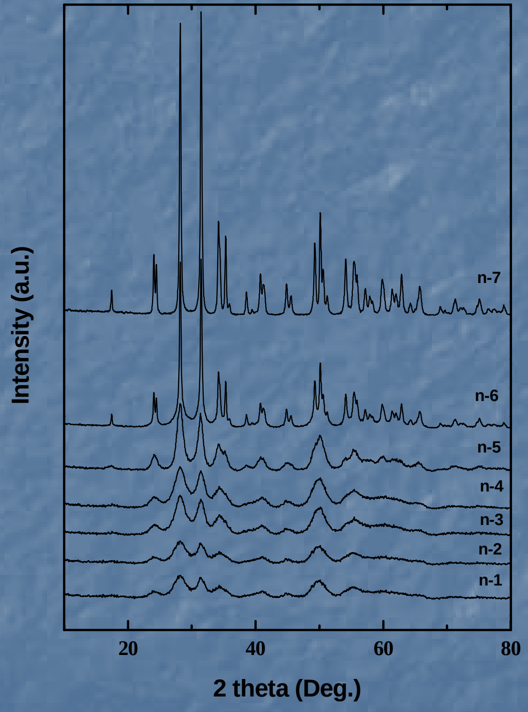
从纳米材料的拉曼散射光谱看动量守恒的变化结果

- 在纳米材料（d<25 nm)中，声子波函数的局域化引起选择定则的迟豫，导致其散射光谱的特征为：

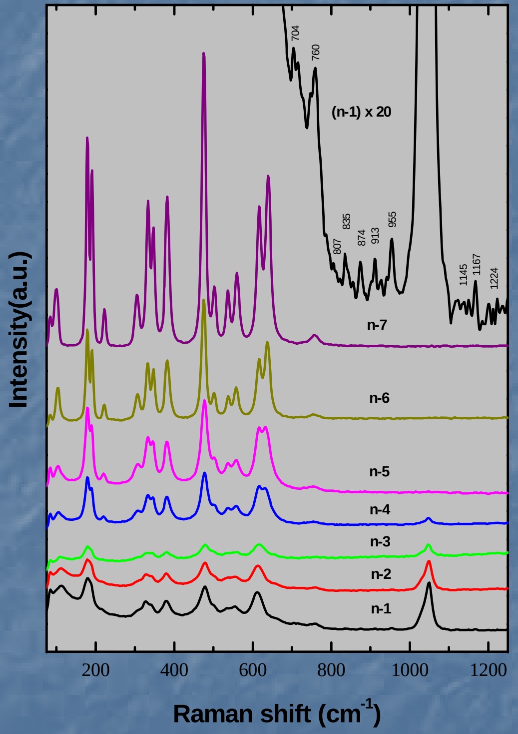
1、拉曼峰的移动。 2、拉曼峰的低频端反对称展宽。

3、表面（界面）声子的出现。 4、高阶拉曼散射的出现。

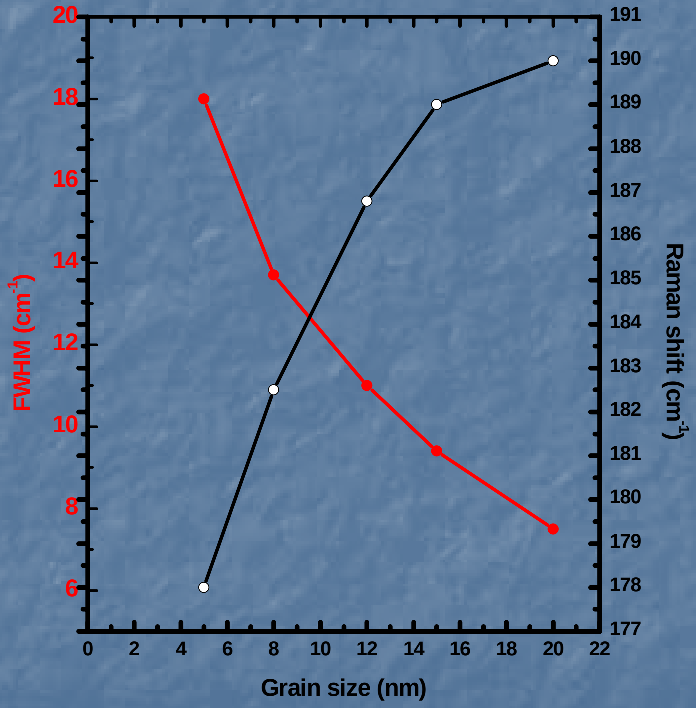
三、非弹性散射的基本特点



不同晶粒尺寸的纳米ZrO$_2$的XRD光谱

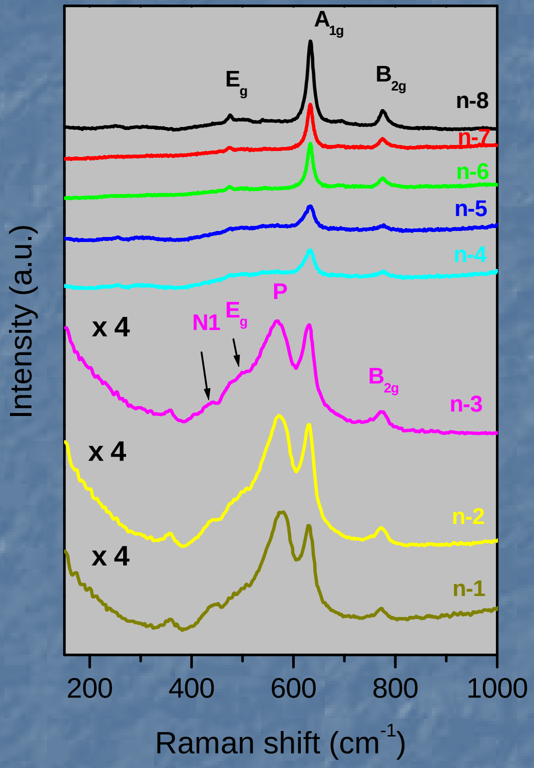


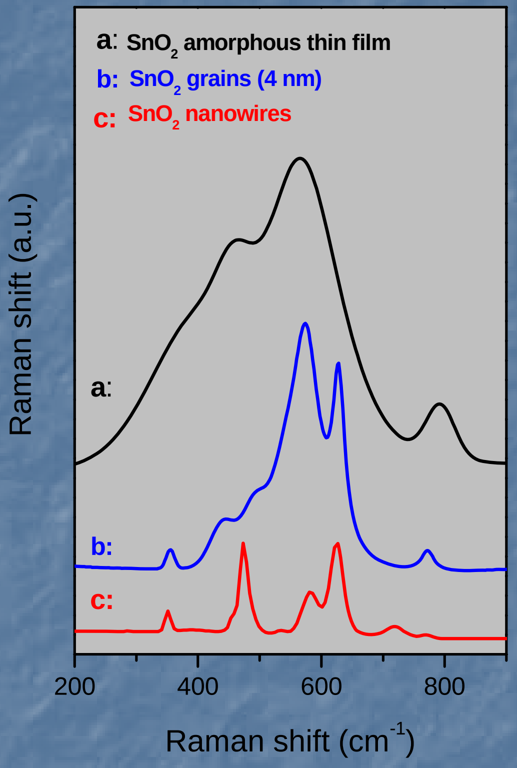
不同晶粒尺寸的纳米ZrO$_2$颗粒的拉曼光谱



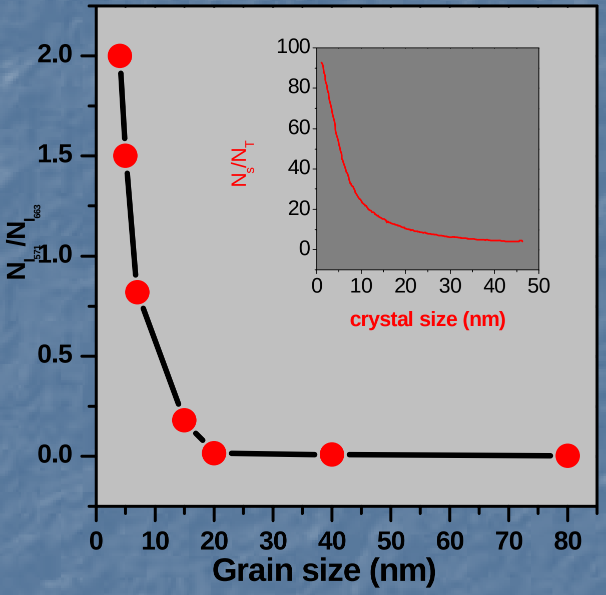
不同晶粒尺寸的纳米SnO$_2$颗粒的拉曼线宽与频移变化

关于纳米SnO_2颗粒中强拉曼峰P的属性指认的实验与理论依据





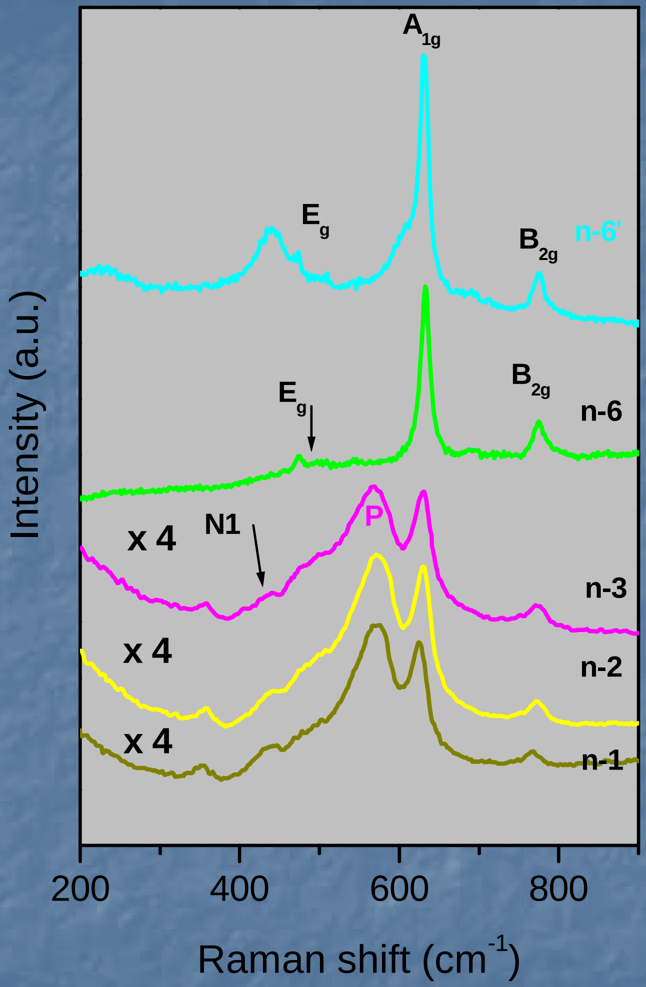
非晶态SnO_2薄膜、纳米SnO_2颗粒和SnO_2纳米线的拉曼光谱

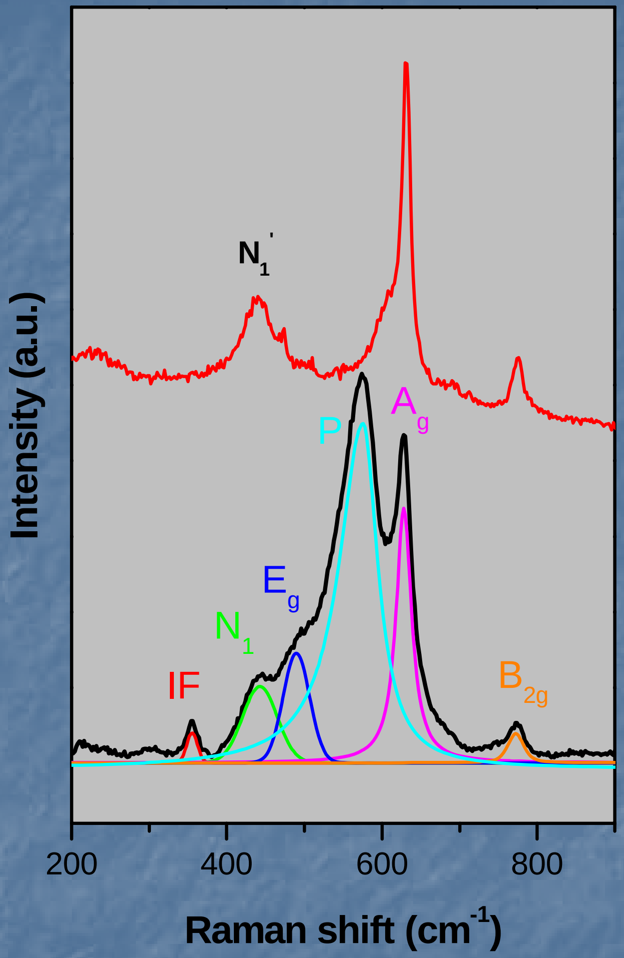


$N_{S(571)}/N_{T(663)}$ 的相对散射强度比与晶粒尺寸的关系

不同制备方法具有不同的微结构

关于纳米SnO_2颗粒中若干弱拉曼散射峰（N_i)的指认





三、非弹性散射的基本特点

随着粒径的减小，庞大的比表面，键态严重失配，出现许多活性中心，使纳米材料具有极强的吸附能力

实例小结

上述举例说明：拉曼散射可以用于材料的鉴定，晶体的完整性的研究等等。

另外以下原因可能造成动量守恒被破坏：

1. 周期性晶格中有缺陷，杂质，或应力。
2、 *固体中原子的排列为无序状态（非晶态）。*
3、 亚铁磁和顺磁相中自旋无序（温度变化）。
4、 *列向无序性（如在NH_4Br中）。*

在这些情况下，整个布里渊区的波矢都参加散射。我们观察到声子的单声子态密度，不同频移下的散射强度往往代表了元激发的态密度。

拉曼光谱仪的组成部分

拉曼光谱仪主要由五个基本部件组成：

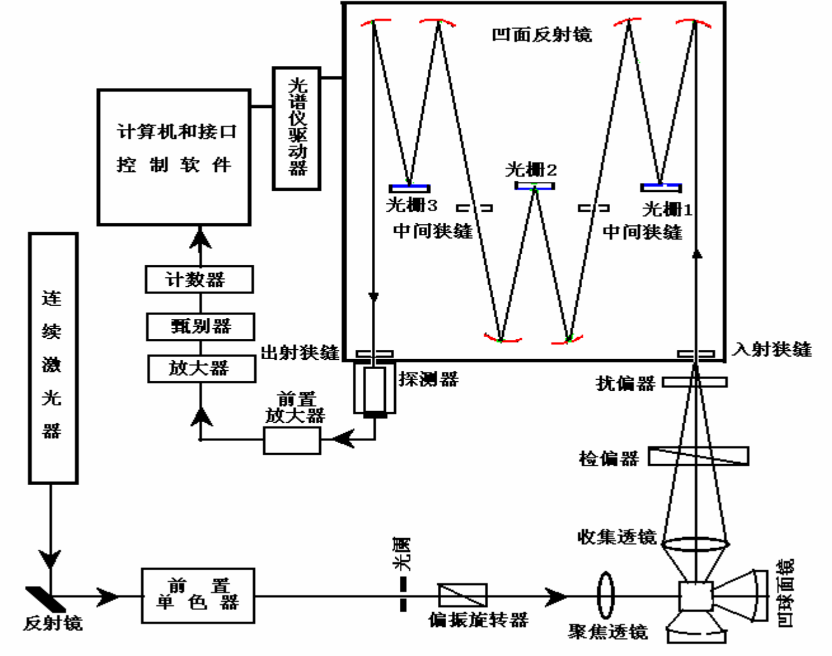
1、用于激发被测样品的激发光源（激光）。

2、收集散射光光学系统。

3、把散射光中不同频率的光分开的分光光度计（单色器）。

4、测量各种不同散射光频率（或说光强）的检测器。

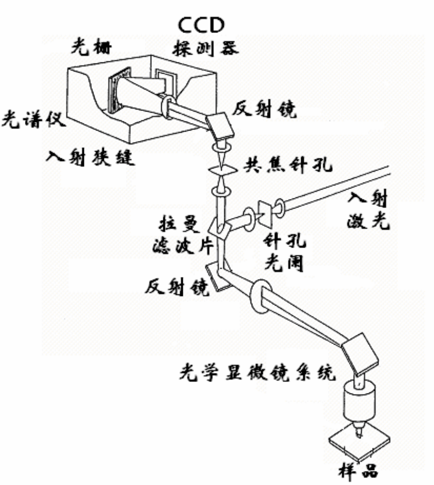
5、用于单色器扫描控制、数据采集/处理和数据分析的操作软件。

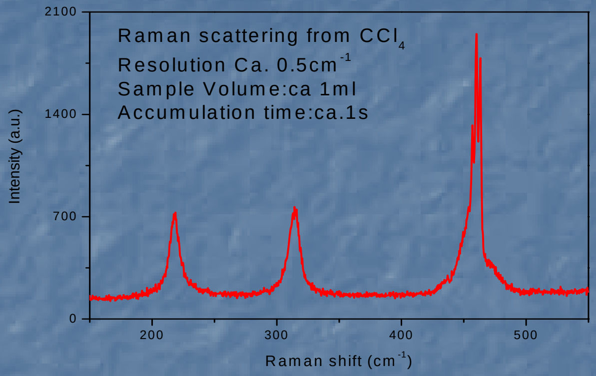


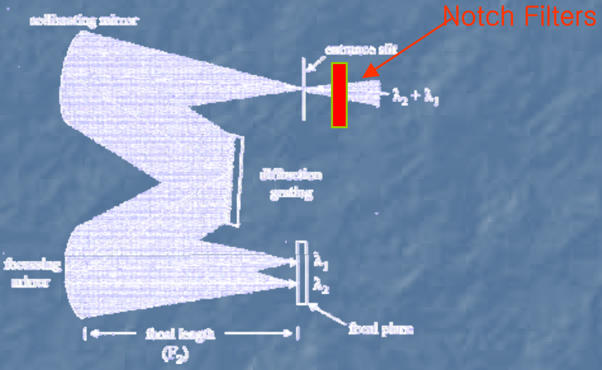
色散型三光栅拉曼光谱仪的示意图

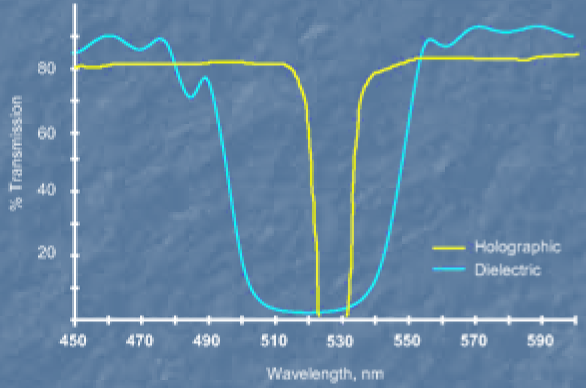
四、拉曼光谱仪构造与进展

小型拉曼光谱仪的基本构造（Laser line rejection – Notch Filters）





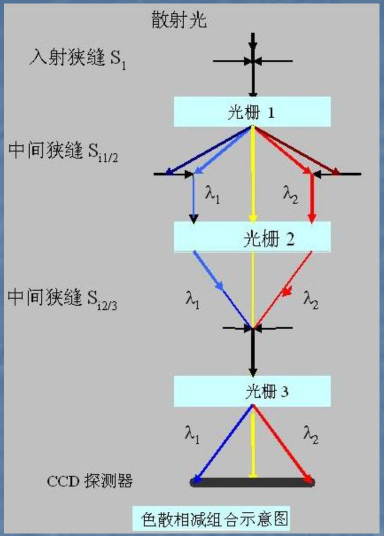


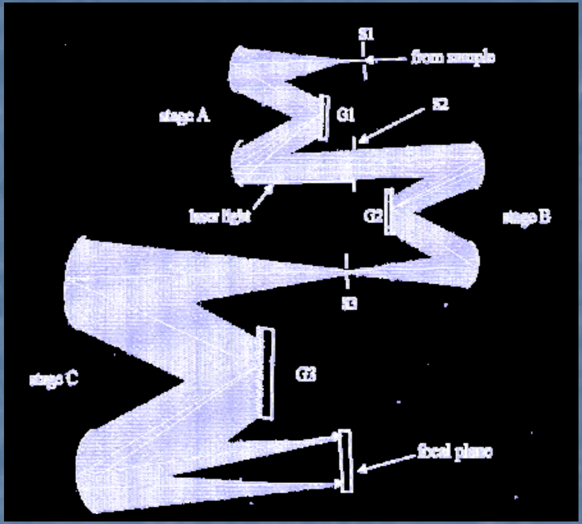


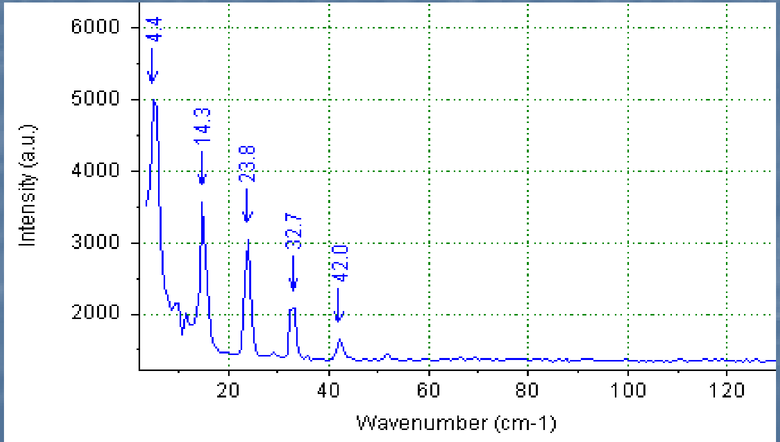
优点：1、对瑞利散射有很强的阻挡能力。2、通光效率高（灵敏高）。
3、能耗低。4、体积小。

缺点：1、不能做低波数的拉曼测量。2、只能做背向散射。
3、不能做共振拉曼的实验。

新型大型拉曼光谱仪：模块式三级单色仪（Spectrometer –Triplemonochromator）







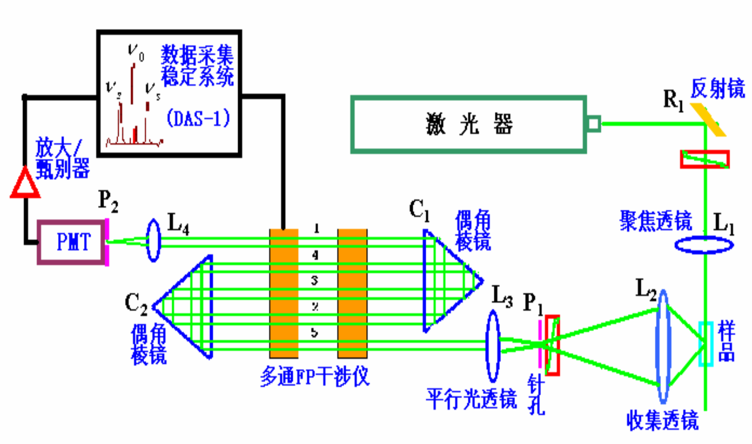
在色散相减模式下，SiGe超晶格材料的折叠声子的拉曼散射光谱

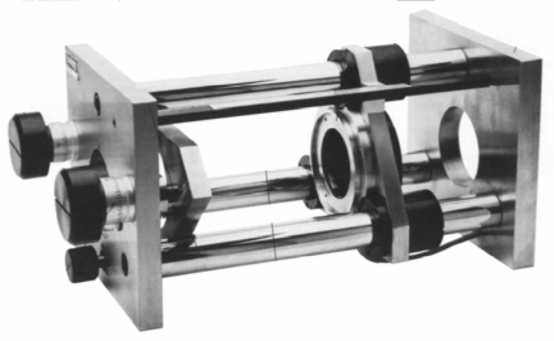
特点： 1、高的光谱分辨率（色散相加）。2、低波数测量色散相减）。3、可做共振拉曼测量。4、可做各种散射配置测量。5、有显微/宏观光路。6、配有CCD/PMT双探测器。

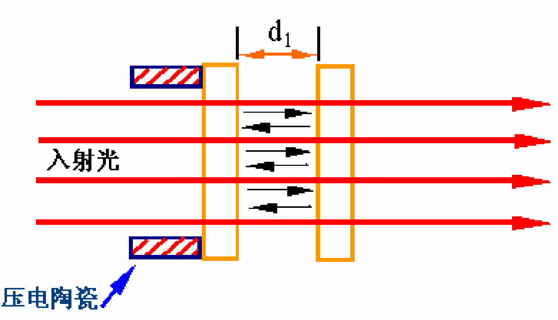
缺点：灵敏度相应低点（相对与小型拉曼光谱仪来讲）。

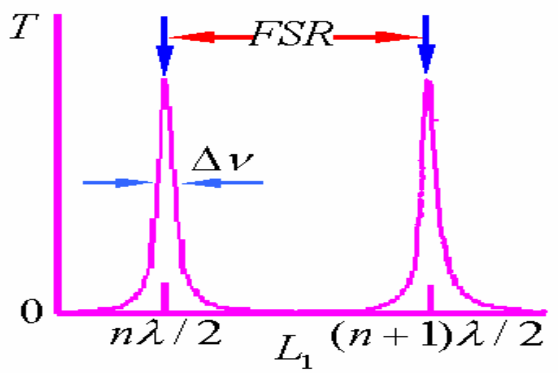
四、拉曼光谱仪构造与进展

布里渊散射光谱仪与Fabry－Perot（FP）干涉仪









光的最大传输：

$$m\lambda = 2nd_1\cos\theta$$

自由光谱区(FSR)：

$$FSR = C_{光速}/2d_1$$

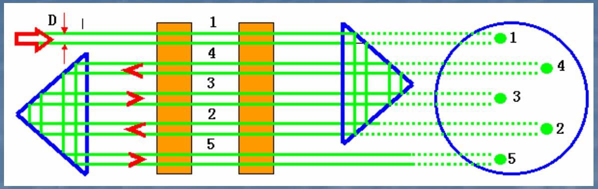
锐度(F,精细度)：

$$F = FSR/\Delta\nu$$

对比度：

$$C = I_{max.}/I_{min.} \approx 4F^2/\pi^2 \leq 10^5$$

Dr. J.R.Sandercoker与 F-P 干涉仪的变革



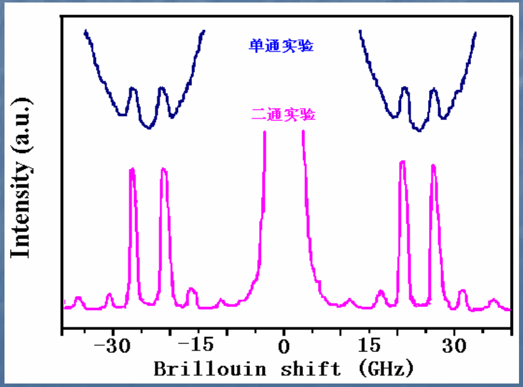
单级多通FP原理图

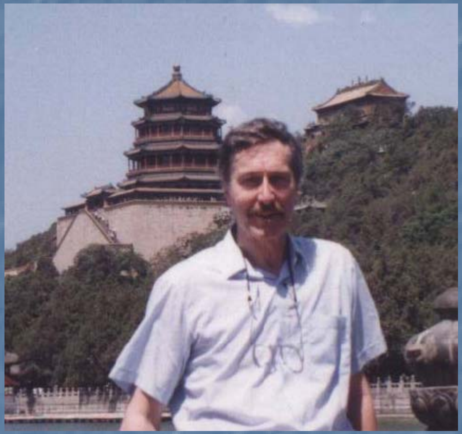
多通FP的对比度：

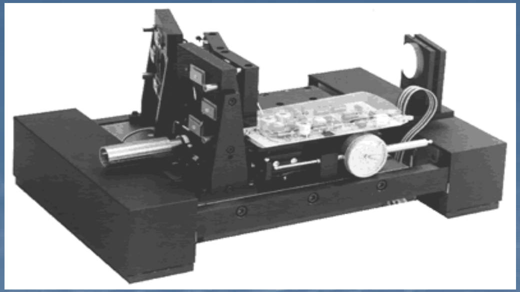
$$C_p = C_1^p$$

多通FP的锐度：

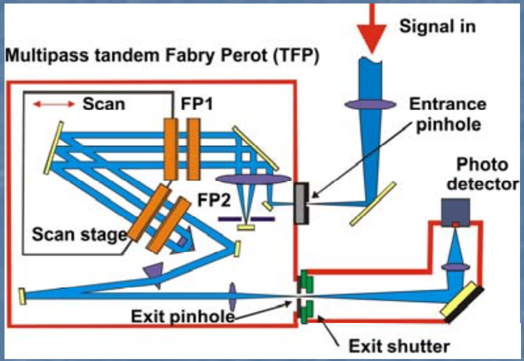
$$F_p = (2^{\frac{1}{p}} - 1)^{-\frac{1}{2}} \cdot F_1$$



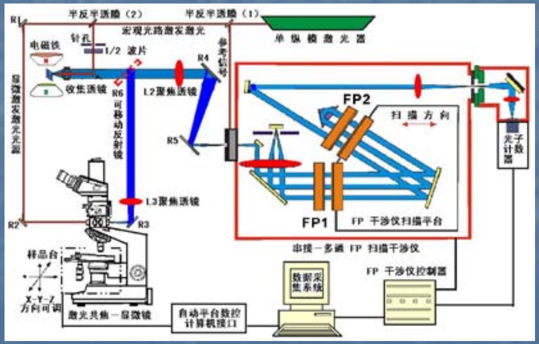




串接多通FP实物图



串接多通FP原理图：



在中科院物理研究所的多功能布里渊散射光谱仪

四、拉曼光谱仪构造与进展

什么是拉曼光谱学？

拉曼光谱学用光与物质相互作用为手段，以晶格动力学，分子光谱学，量子力学，群论和各专业知识为基础理论，运用激光技术、光学精密机械、弱光检测技术，及计算机技术为一体，应用遍及物理、化学、生物、环境、材料，生命，地矿，刑侦，考古等领域的综合学问。

拉曼光谱学的核心：

一个原理－动量守恒和能量守恒

两类散射－拉曼散射和布里渊散射

三种散射配置－直角散射，背向散射，前向散射

三个重要参量：振动频率(ν),散射强度(I),和线宽(Γ)

五、拉曼光谱学及其应用

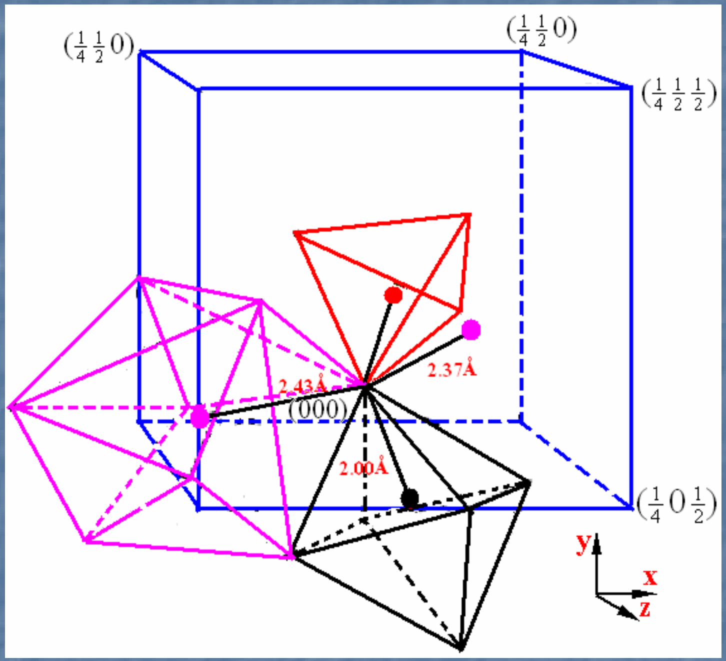
Light Scattering from Magnons and Phonons in $Y_{3-x}Bi_xFe_5O_{12}$ (Bi-YIG) Single Crystals

1. Bi-YIG structure and their applications
2. Brillouin light scattering from Bi-YIG crystals
3. Raman scattering from Bi-YIG crystals
4. summary

五、拉曼光谱学及其应用

The crystal structure of $Y_{3-x}Bi_xFe_5O_{12}$

Yttrium iron garnets of the composition $Y_3Fe_5O_{12}$ (YIG), which is a typical ferrimagnet, have been important to microwave and magneto-optic technology.



The structure of $Y_3Fe_5O_{12}$

$\{Y_3\}^c[Fe_2]^a(Fe_3)^d O_{12}$ (YIG)

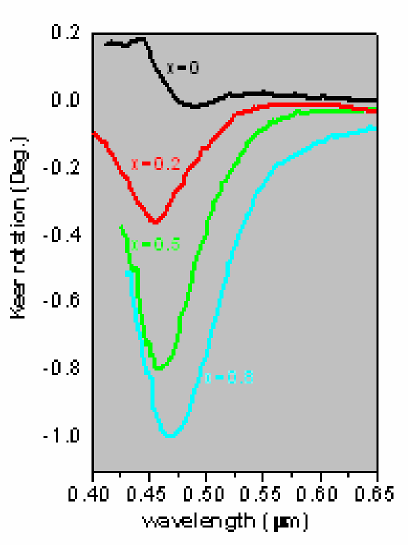
$\Updownarrow$ doping Bi^{3+}

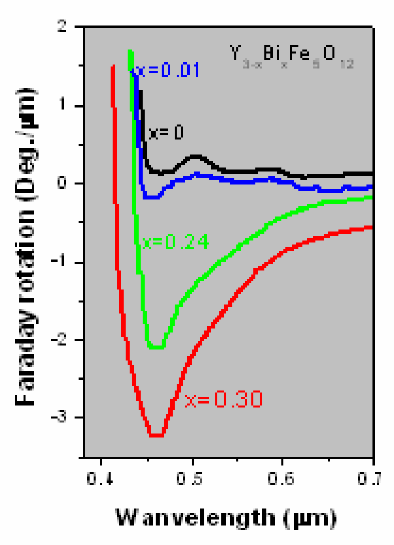
$\{Y_{3-x}Bi_x\}^c[Fe_2]^a(Fe_3)^d O_{12}$ (Bi-YIG)

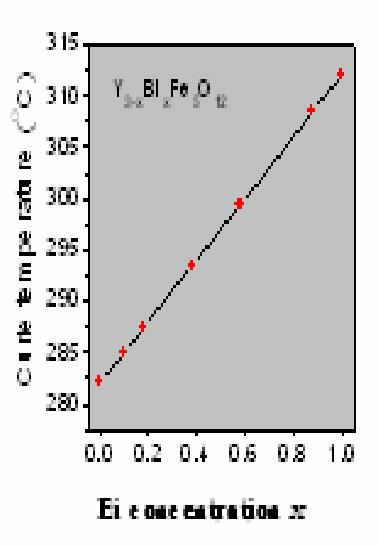
- ● Fe^{3+} (octahedral, a sites)
- ● Fe^{3+} (tetrahedral, d sites)
- ● Y^{3+} (dodecahedral, c sites)

The Faraday rotationθ_F and Keer rotationθ_K, as well as the Curie temperature,of Bi-YIG increase with the Bi concentration.

Bi-YIG







The magneto optic –enhanced effects on Bi-YIG have attracted considerable experimental and theoretical interest in the past, various mechanism of the effects proposed. The physical origins of these effects are not clear so far. Thorough theoretical and experimental description to their origins is still needed.

Mainly different opinions:

1. **New type of transitions in Bi-YIG have been appeared**
2. **The substitution of Y with Bi in YIG may relax the selection, initially forbidden transitions in YIG are possible or allowed transitions are srengthened.**

五、拉曼光谱学及其应用

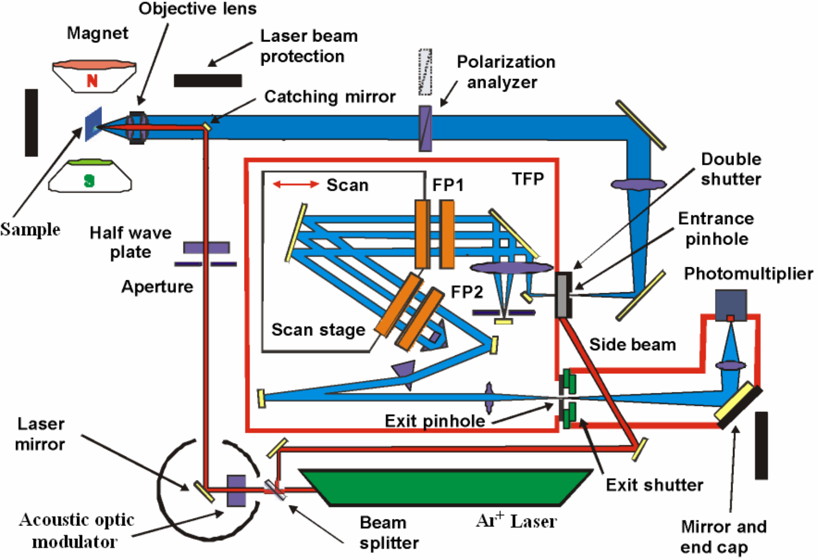
Experiment: samples and their compositions

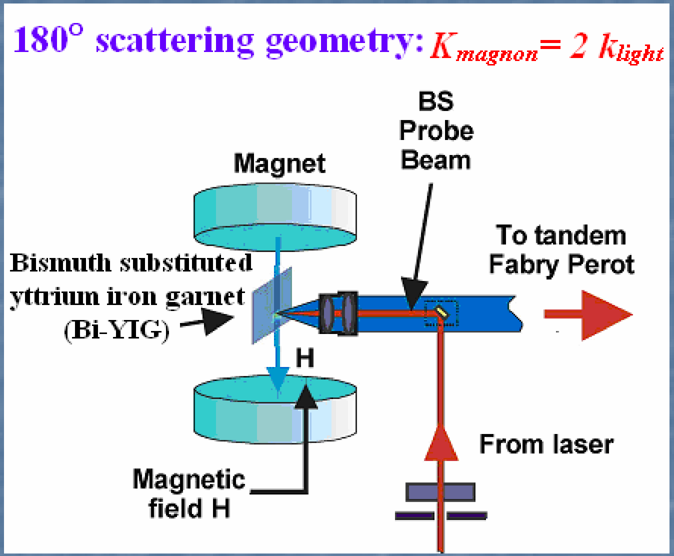
Bi-YIG single crystals were grown by the flux method. The melt of constituent oxides with Bi_2O_3-PbO-B_2O_3 as flux was slowly cooled in Pt crucible.

Five slab samples cutting from bulk crystals with x=0, 0.14, 0.36, 0.54 and 0.92, respectively, all of size ~2.0x2.x0.5mm^3, are selected for Brillouin light scattering.

五、拉曼光谱学及其应用

Experiment: equipments and scattering geometry




180° scattering geometry: $K_{magnon} = 2\ k_{light}$

A JRS tandem Fabry-Perot interferometer (3+3 systems) for BLS

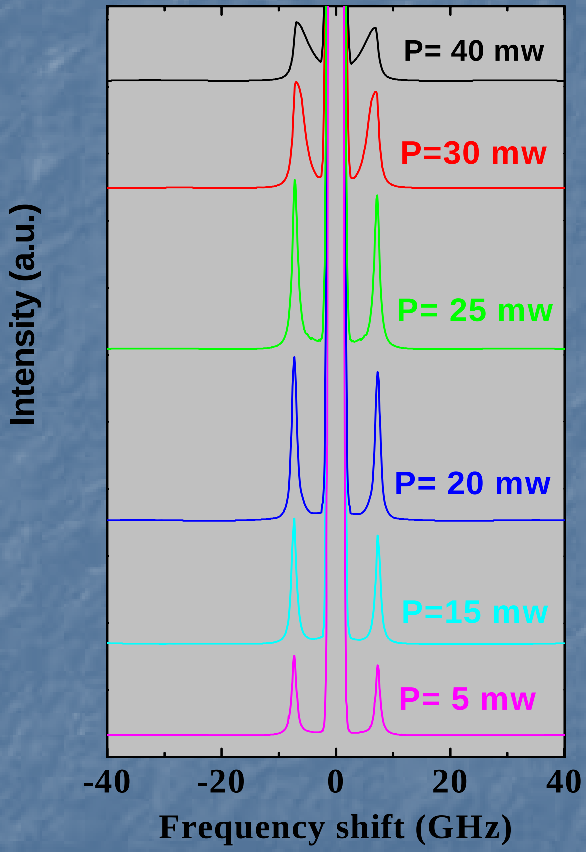
Back scattering: The optic axis of a focusing and collecting lens is taken to be the x axis. The sample slab stands vertically on the holder in the gap of a magnet and its surface normal coincides with the axis.

五、拉曼光谱学及其应用

The broadening and downshift effect of laser power on magnon

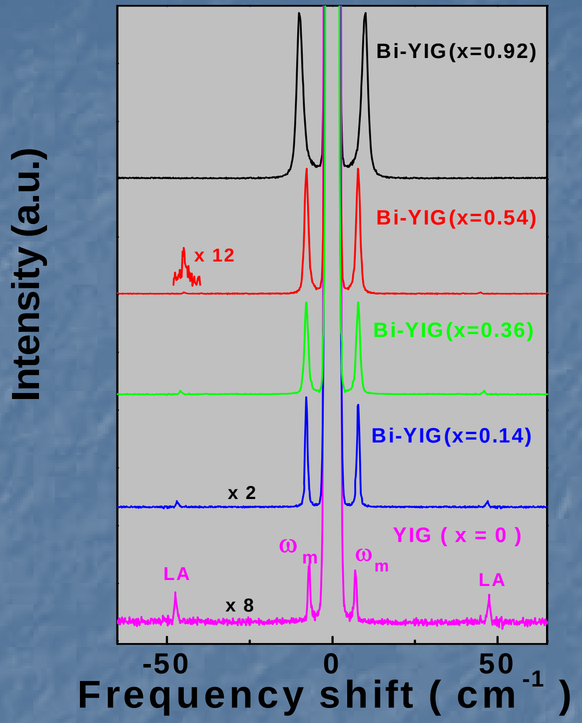
When laser power exceeds 25 mW, the spectra deteriorate drastically: the peaks weaken and widen markedly with decreasing frequency shift and intensifying anti-symmetry. It shows that large-power excitation could affect the magnetic order of the crystal Bi-YIG and produce widening of spectral lines.

Low power of 5 mW was used and the results were good.

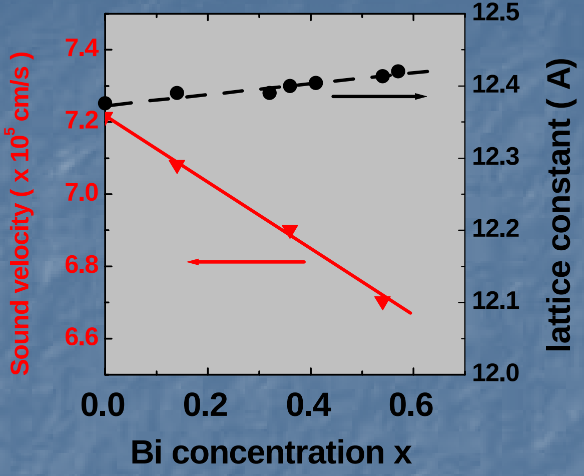


BLS spectra of single crystal Bi-YIG (x=0.14) at different excitation power

Effect of Bismuth concentration on sound velocity



BLS spectra of Bi-YIG with different x at *H=0* at 5 mW excitation. The spectra show that the intensity and frequency of the LA phonon decrease with *x* while the magnon intensity and frequency increase with *x*.



Bi-concentration dependences of the sound velocity of the LA phonon propagating along (red) and the lattice constant of Bi-YIG

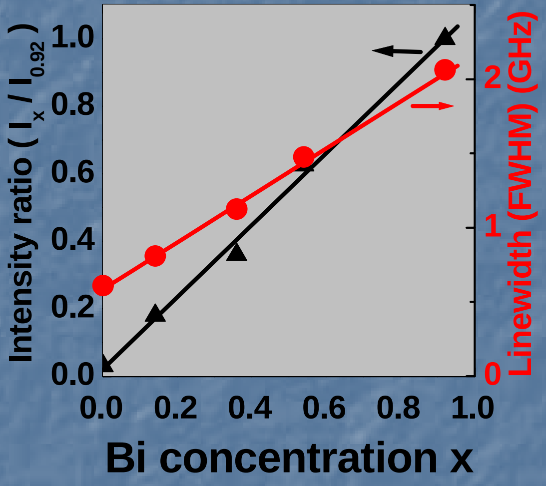
The LA sound velocity V_L: $k = \frac{4\pi n}{\lambda}$

$$V_L = \frac{\omega_p}{k} \quad ;$$

V_L=7.18x10^5 cm/s for YIG

V_l =6.71x 10^5 cm/s for Bi-YIG (x=0.54)

Scattered intensity and the band width of bulk magnons



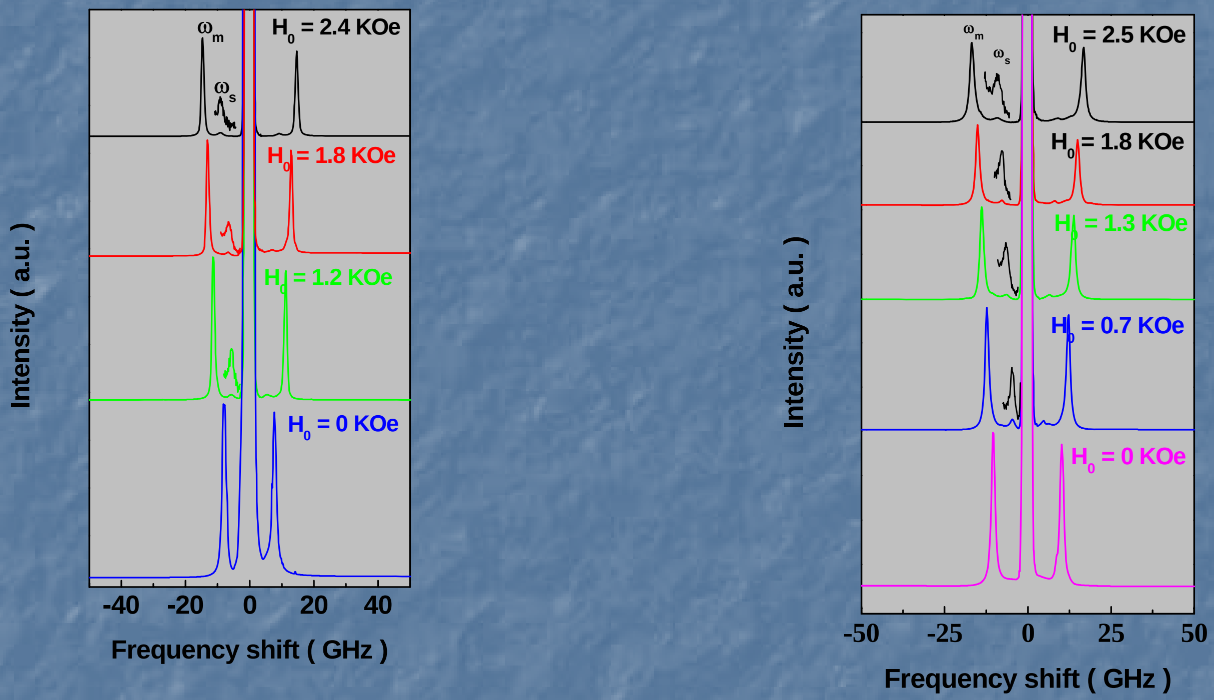
Bi-concentration dependences of the bulk-magnon relative intensity and linewidth (triangles and full circles)

The scattered intensity of Bi-YIG at $x = 0.92$ is taken as the reference. The relative intensity of Bi-YIG vs the concentration x is shown in the figure. The scattered intensity increases linearly with x.

The bandwidth of bulk magnons at ~1.8Koe is fitted using the standard Lorentzian line shape. Δf increases from 0.60 GHz at $x = 0$ to 0.81,1,12,1.48,and 2.06, all in unit of GHz, for x = 0.14,0.36,0.54, and 0.92, respectively.

五、拉曼光谱学及其应用

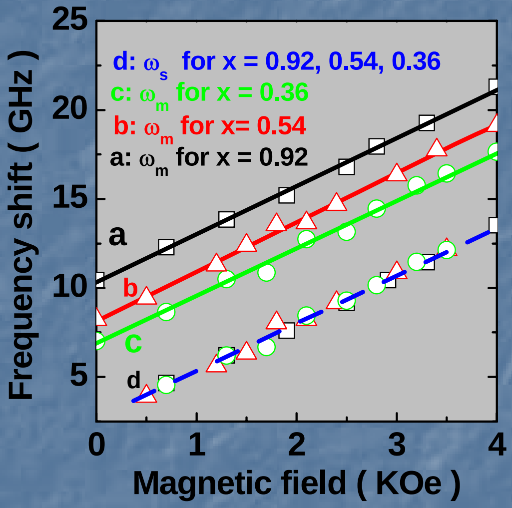
Polarized BLS spectra of magnons from Bi-YIG as the external magnetic field H_0.


(a) Bi-YIG (x=0.92)

(b) Bi-YIG (x=0.54)

ω_s is determined to be scattering from magnon too by varying external field and scattering polariztion.

The stiffness constant D_{ex} in Bi-YIG



Magnetic-field dependence of the bulk magnons frequencies ω and the weak peaks in Bi-YIG at 514.5 nm excitation. The squares, triangles, circles are data for x=0.92, 0.54,and 0.36,respectively, the solid lines are fited from Eq.(2)

The magnon frequency ω_m should be related to the effective magnetic field H_0 and the magnon wavevectork_m, for $k_m \perp H_0$, by the dispersion relation:

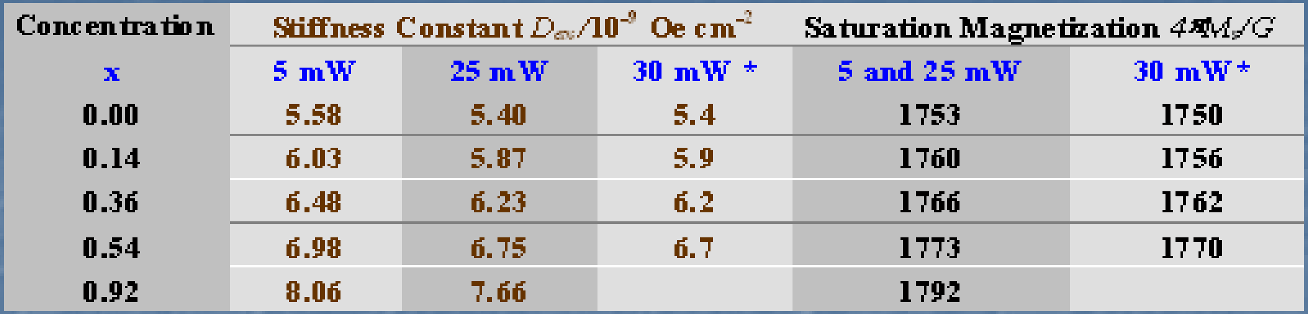
$$\omega_m = \gamma^2 \sqrt{(H_0 + D_{ex}K_m^2)(H_0 + D_{ex}K_m^2) + 4\pi M_s} \qquad (1)$$

γ is the gyromagnetic ratio, H_0 should the external field and both the anisotropic field and demagnetizing field (H_0 = $H_{appl.}$+H_{an} +$H_{demag.}$) . D_{ex} is the spin wave exchange stiffness constant and $4\pi M_s$ is the saturation magnetization. D_{ex} and $4\pi M_s$ are taken as parameters fitted to the experimental data.

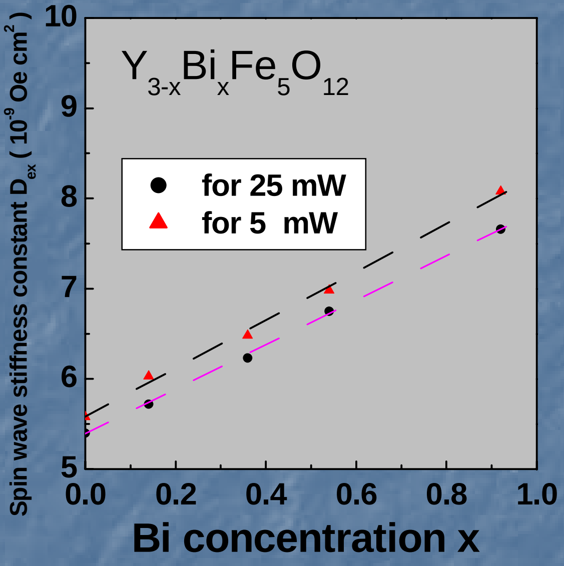
The dispersion relation for our experiment:

$$\omega_m \approx \gamma[H_0 + D_{ex}K^2 + (1-2N)2\pi M_s] \quad (2)$$

TABLE 1. The stiffness constant D_{ex} and saturation magnetation $4\pi M_s$ in Bi-YIG



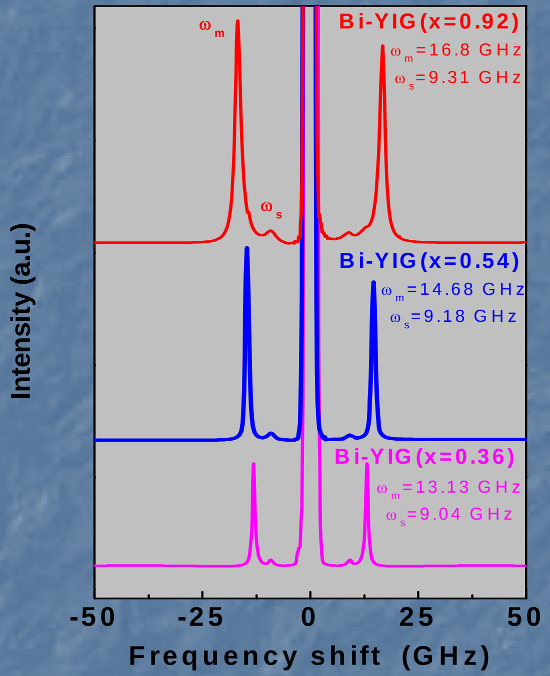
Concentration	Stiffness Constant $D_{ex}/10^{-9}$ Oe cm^{-2}			Saturation Magnetization $4\pi M_s/G$	
x	5 mW	25 mW	30 mW *	5 and 25 mW	30 mW *
0.00	5.58	5.40	5.4	1753	1750
0.14	6.03	5.87	5.9	1760	1756
0.36	6.48	6.23	6.2	1766	1762
0.54	6.98	6.75	6.7	1773	1770
0.92	8.06	7.66		1792	



Bi-concentration dependence of the spin-wave stiffeness constant D_{ex} under 5 and 25 mW, respectively.

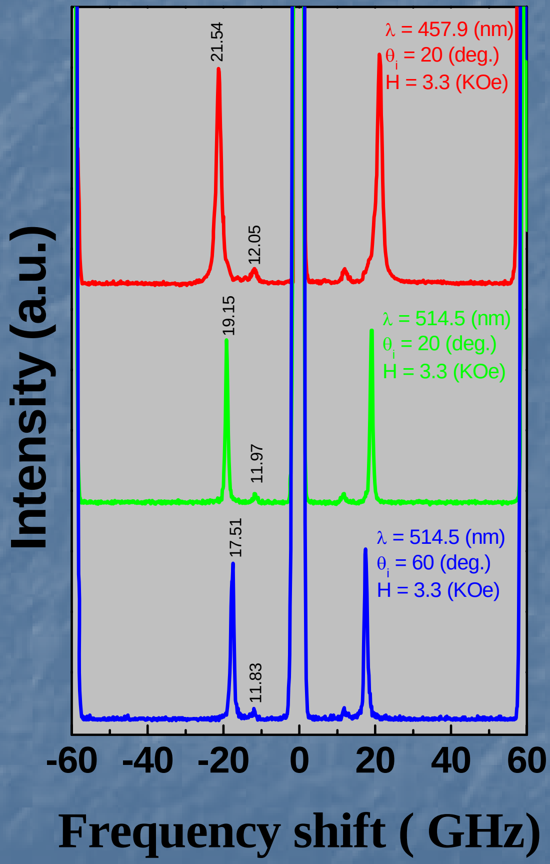
New weak peak ω_s in Bi-YIG

1. Could it be a surface magnon? 2. Could it be a kind of density-states effects of magnon ?



BLS spectra of the bulk magnon ω_m and weak peak ω_s for different Bi concentration in exteral magnetic field of 2.5 kOe.

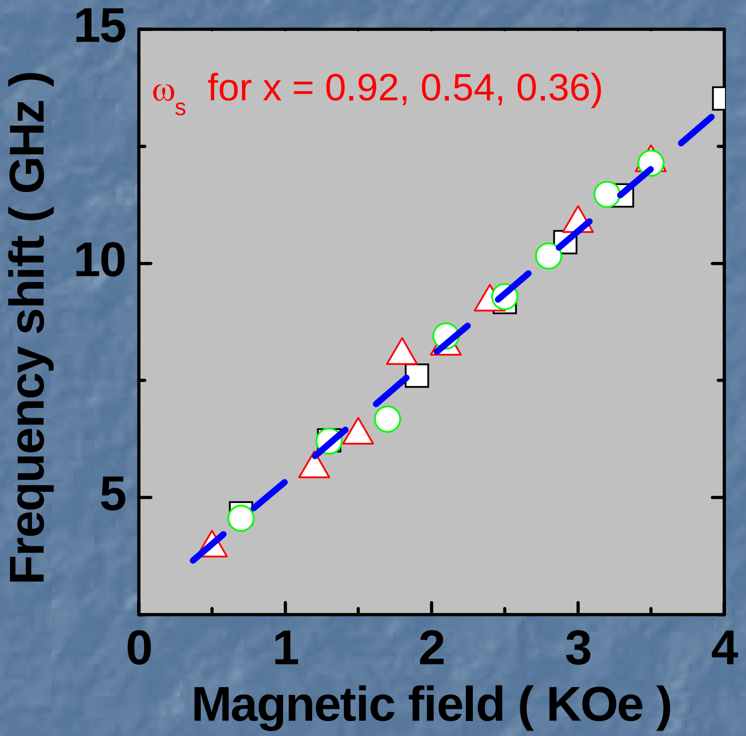
BLS spectra of magnons of Bi-YIG (x=0.92) at 457.9 nm (θ_i=20°;H =3.3 kOe) and 514.5 nm (θ_i=20°, 60°; H =3.3 kOe) excitations, respectively



The frequency of surface magnon ω_s could be determinted according to the theory of surface magnon.

$$\omega_s = \gamma[H + 2\pi M + \xi D_{ex} k_y^2]$$

Magnetic-field dependence of the weak peaks in the Bi-YIG at 514.5 nm. The squares, triangles, and circles are data for x= 0.92, 0.54,and 0.36 . The dash line is fitted from the formula.



$$\omega_s = \gamma\sqrt{H_0(H_0 + 4\pi M_s)}$$

3. Raman scattering from Bi-YIG crystals

The enhancement of the magneto-optic coupling owing to The Bi-doping makes an opportunity of optic magnon in the magnetic materials.

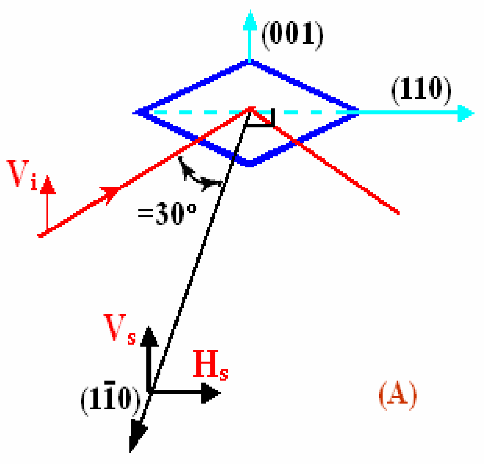
The result will provide useful information for studying the relationship between the Bi concentration, the microstructure of Bi-YIG crystals, and their magnetic and mechanical properties if the magnon is found.

The crystal structure of Bi-YIG and Raman active phonons:

The crystal structure of Bi-YIG belong to the space group O_h^{10} (Ia3d), isomorphic to that of YIG. Since contains the inversion operator, the $K = 0$ phonons are either infrared active ,Raman active, or silent. There are 25 Raman active phonons which can be classified as 3A1g + 8Eg + 14T2g

五、拉曼光谱学及其应用

Crystal orientation and selection rules



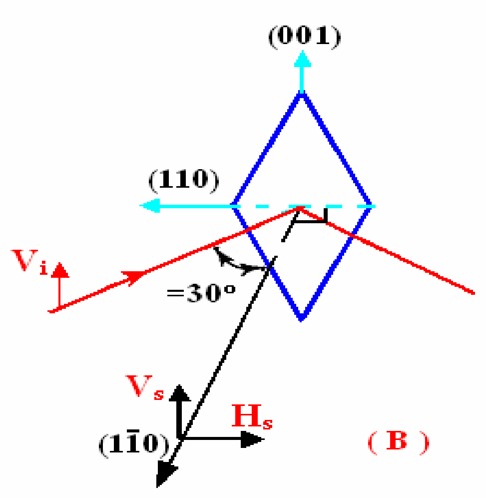
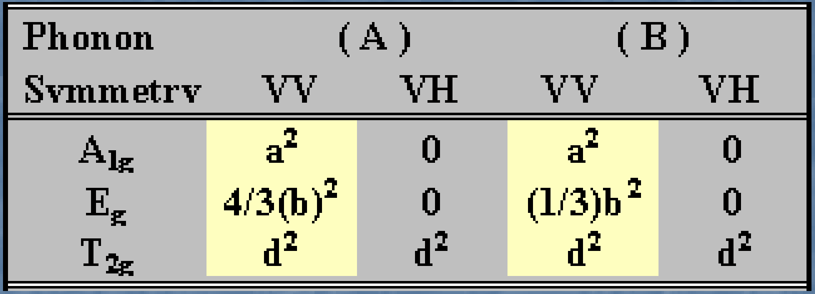


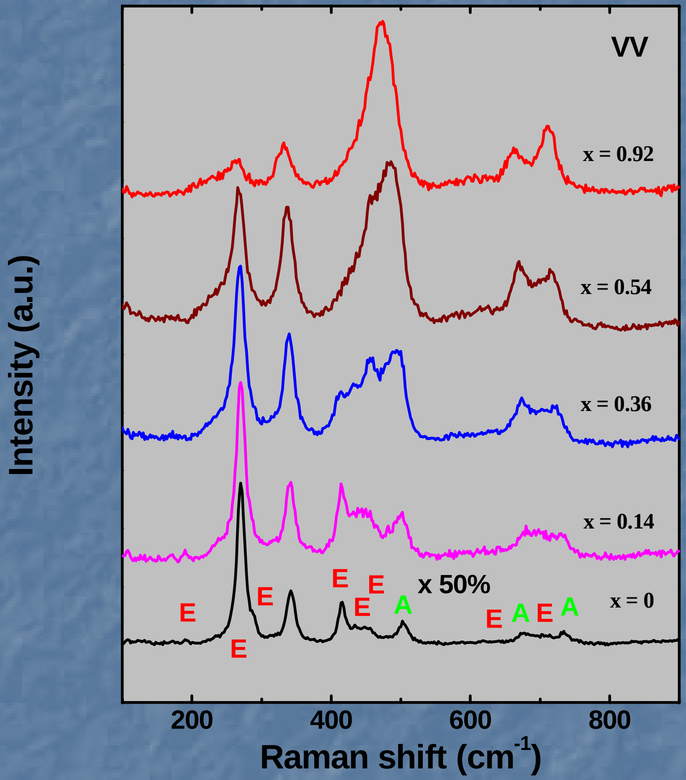
Table: Relative phonon Raman intensities for crystal orientations shown in geometry (A) and (B)

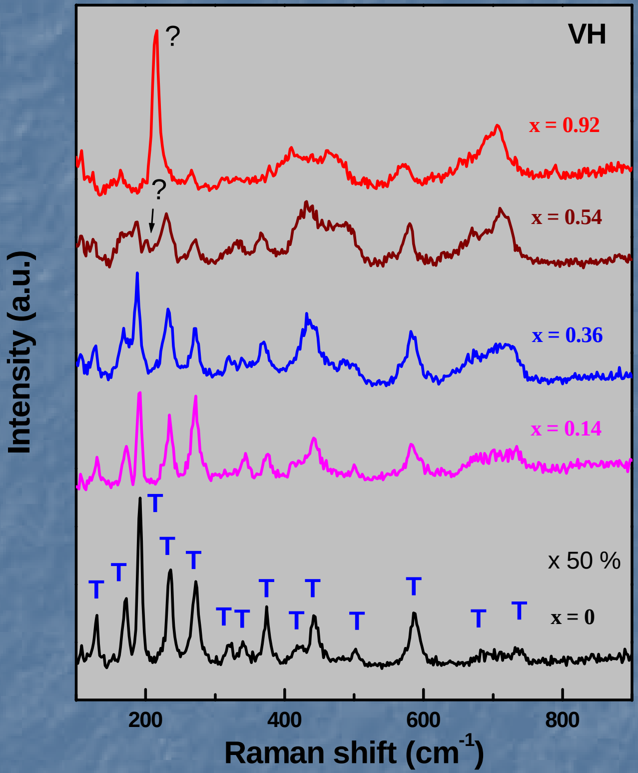


Phonon	(A)		(B)	
Symmetry	VV	VH	VV	VH
A_{1g}	a^2	0	a^2	0
E_g	$4/3(b)^2$	0	$(1/3)b^2$	0
T_{2g}	d^2	d^2	d^2	d^2

Here V and H refer to the direction of the polarization as being in either the vertical or horizontal planes, respectively. The subscripts, *i* and *s*, refer to the incident and scattered light, respectively.

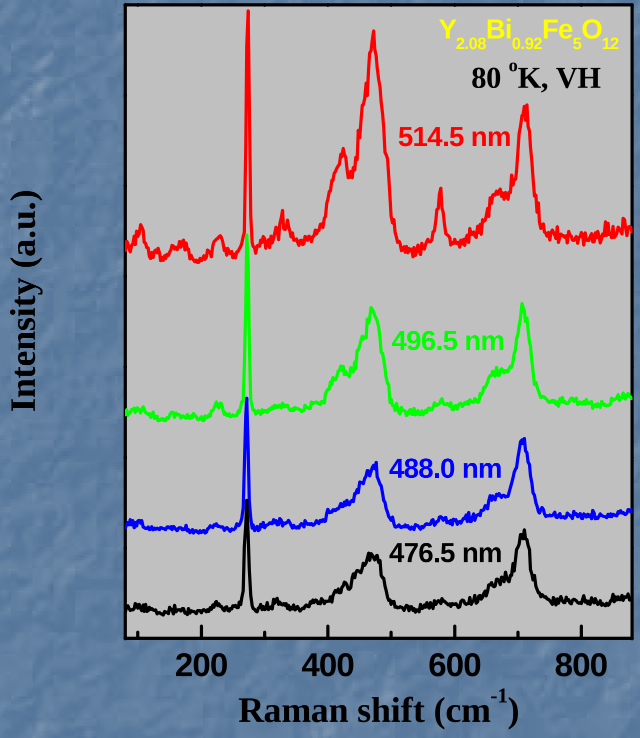
Polarized Raman spectra of Bi-YIG with Bi-concentrations x = 0, 0.14, 0.36,0.54 and 0.92 at room temperature using 514.5 nm argon emission





What is the new peak in Bi-YIG(x= 0.54, 0.92) ?

Raman spectra of Bi-YIG (x=0.92)with four different laser lines at 100 ° K



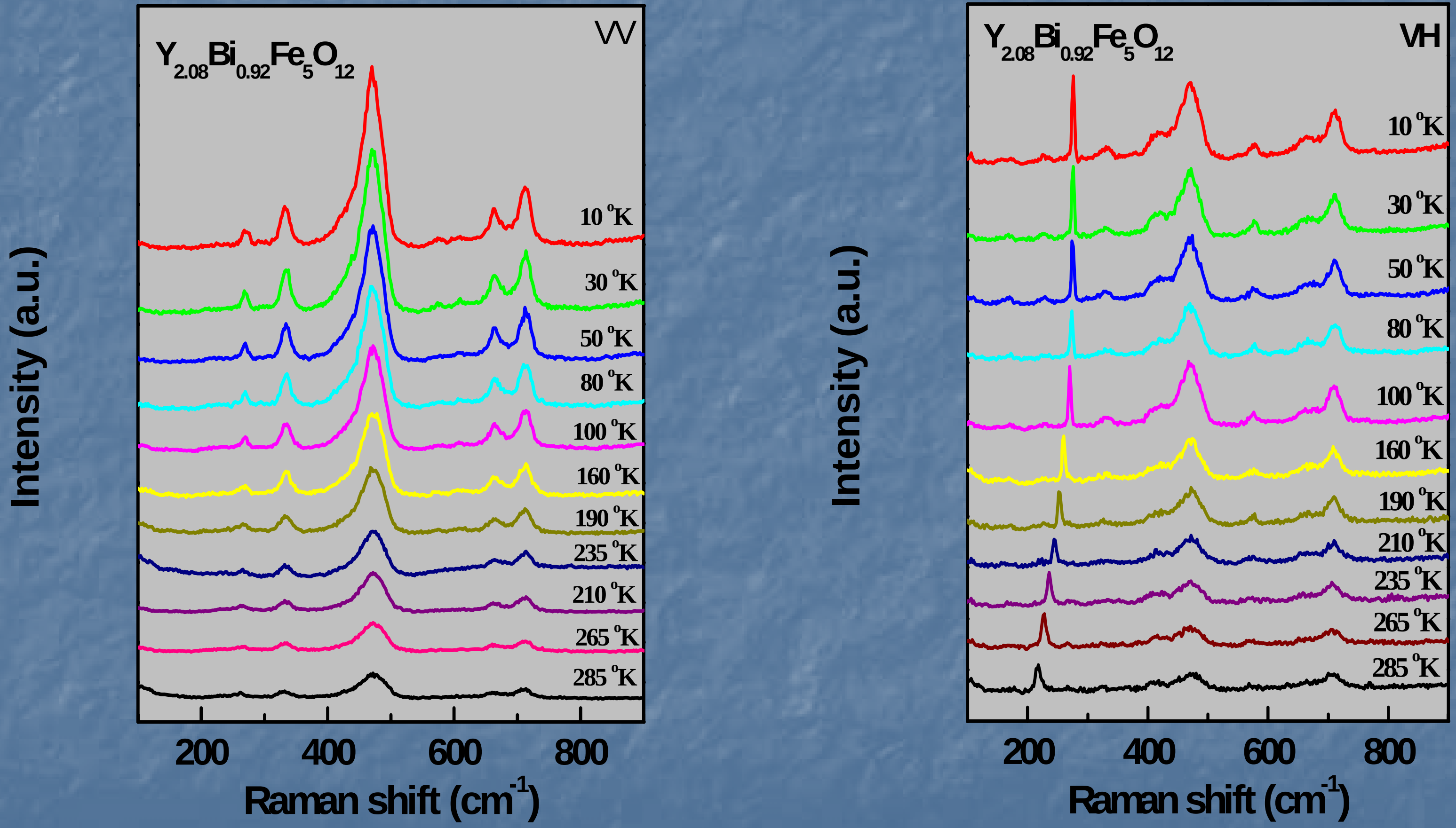
Raman data were taken with four different laser lines from argon laser, in order to eliminate misidentification of our Raman data duo to possible fluorescence from trace impurities.

Finally, the observed process is indeed a first order scattering rather than a fluorescence was confirmed by observing the anti-Stokes line at 40 ° K, where $\hbar\omega / kT \approx 2$.

Could it be a electronic Raman scattering or optical magnon?

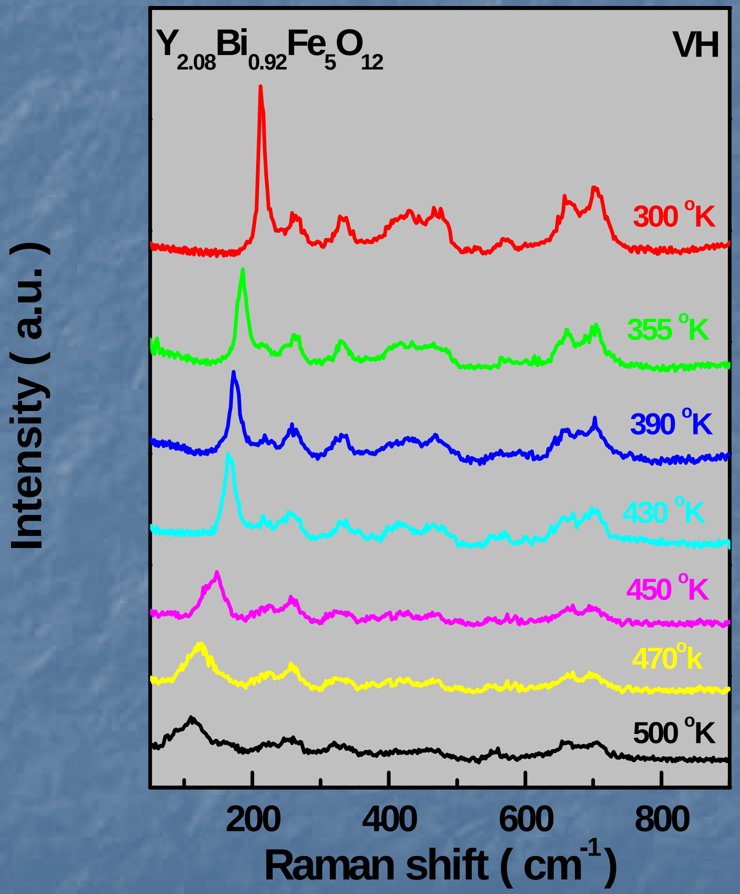
五、拉曼光谱学及其应用

Polarized Raman spectra of Bi-YIG (x=0.92)measured at various temperatures between RT and 10 °K in VV and VH scattering geometry

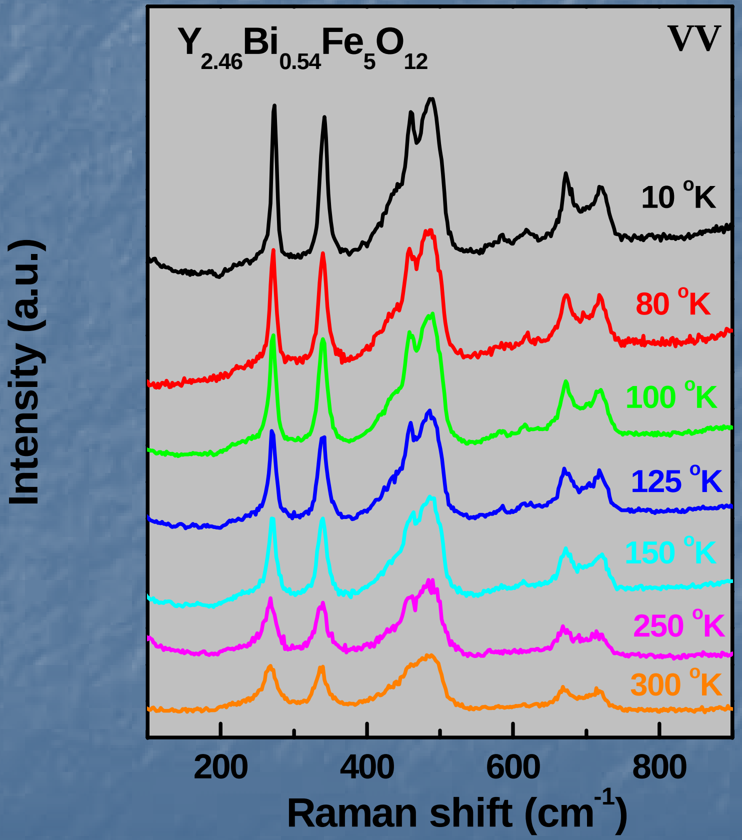


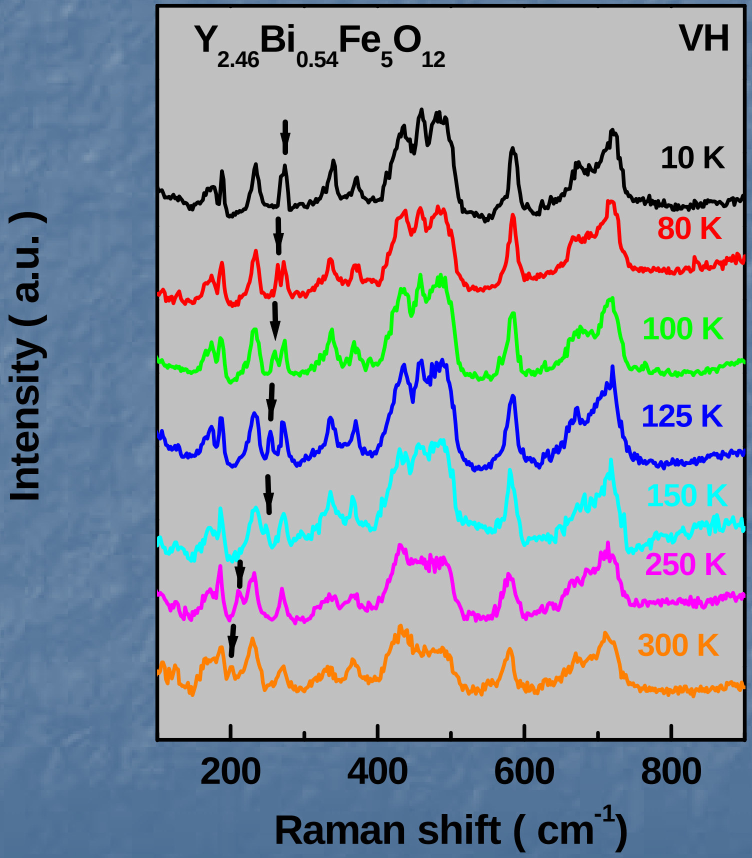
五、拉曼光谱学及其应用

Polarized Raman spectra of Bi-YIG(x=0.92) measured at higher temperatures in VH scattering geometry

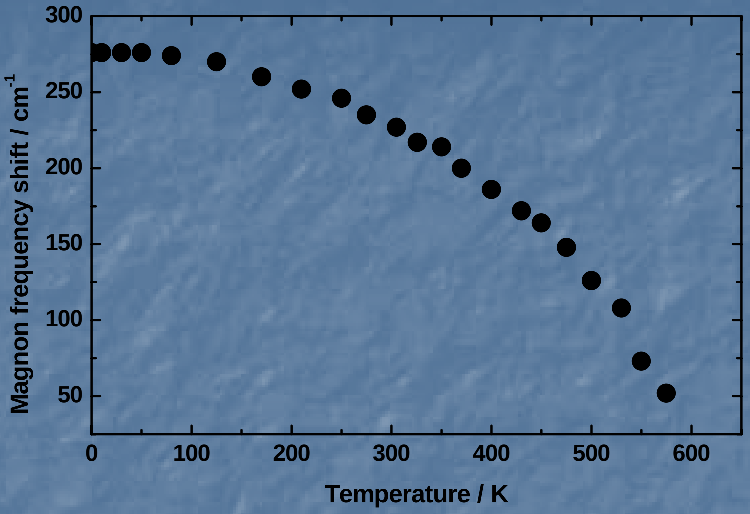


Polarized Raman spectra of Bi-YIG (x=0.54)measured at various temperatures between RT and 10 ^{0}K in VV and VH scattering geometry





Temperature dependence of Stokes frequency shifts in Bi-YIG (x=0.92)



More detailed evidence for the identification of the one-magnon process is given by the temperature dependence and symmetry properties of the scattered light:

1. The position of the 273 cm^{-1} peak is plotted versus temperature.
2. Both the magnitude and temperature dependence of the shift indicate that the scattering is due to a single zone-center magnon.
3. We observe that the peak at 273 cm^{-1}, the nonzero elements are α_{yz} and α_{zy}.

These observations agree with the selection rules obtained by Y. R. Shen.

Approximative calculation of the exchange resonance magnon

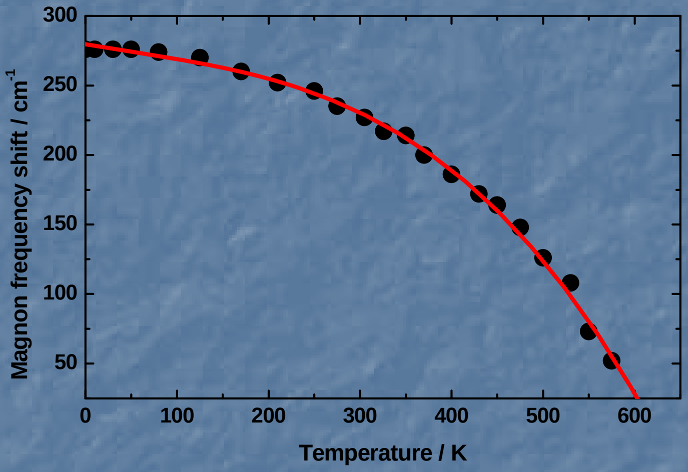
The exchange resonance frquency between two sublattice was derived by Kaplan and Kittel

$$\omega_m = \lambda(\gamma_2 M_1 - \gamma_1 M_2) \qquad (1)$$

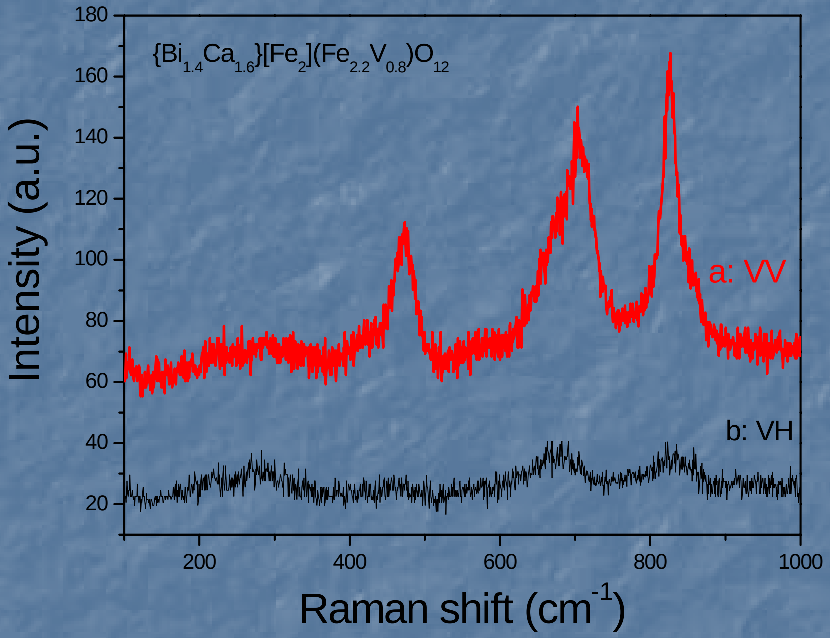
where is λ the molecular field constant; γ_1, γ_2 the respective gyromagnetic ratios; and M_1, M_2; the sublattice magnetizations.

$$\omega_m = \gamma H_E, \qquad (2)$$

$H_E = \lambda M(t)$ is the exchange field . M is the average sublattice magneization. λ can be calculated from the experimentally measured quantities.



Raman scattering from $\{Bi_{1.4}Ca_{1.6}\}[Fe_2](Fe_{2.2}V_{0.8})$ single crystal



The substitution Y with Bi decreases the intensity of Raman shift in the range of the lower frequency .

The appearance of the exchange resonance magnon not only depends on the Bi concentrations in the crystal but also on the exchange interaction between the octahedral sites and tetrahedral sites.

五、拉曼光谱学及其应用

Summary

1. In BLS, the spin wave exchange stiffeness constant $D_{ex}$is very sensitive the excitation power so that low power should used.
2. The behavior of the bulk magnon is opposite to LA phonons.
3. Not only the spin wave exchange stiffness constant, but also the relative intensity and the bandwidth of bulk magnon increase linearly with x.
4. The substitution Y with Bi softens the crystals and the measured sound velocities of the acoustic phonons decrease linearly with x.
5. As an external field is applied, the uniform magnetostatic mode appears.
6. In Raman scattering, the exchange resonance magnons are firstly observed in Bi-YIG($x > 0.54$).

Summary

7. The appearance of the exchange resonance magnon not only depends on the Bi concentrations in the crystal but also on the exchange interaction between the octahedral sites and tetrahedral sites.

Thank you!