



利用光学二次谐波产生表征技术研究反铁磁体

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摘要 反铁磁体/反铁磁材料因其独特的磁性质和在信息存储、自旋电子学和量子计算等领域的潜在应用前景而备受关注。然而, 由于其内部相邻自旋方向相反排列, 导致宏观磁化强度为零, 这使得反铁磁体中磁有序的探测和表征极具挑战性。光学二次谐波产生(second harmonic generation, SHG)技术作为一种高灵敏度、非侵入性的表征手段, 能够高效地探测反铁磁体系的空间反演对称破缺、自旋排列及其相变行为, 现已成为探测表征反铁磁体物性的重要工具。本文综述了光学SHG技术在反铁磁性研究中的应用, 包括其基本原理、实验方法以及在不同反铁磁材料系统(如氧化铬、铁酸钡和二维体系等)中的应用实例。特别关注了SHG技术如何揭示反铁磁体的相变特性、自旋排列、磁畴结构、磁电耦合效应以及在外场作用下的动态响应等。通过这些探讨, 本文旨在突出SHG技术在反铁磁微观机理研究领域的广泛应用前景和巨大优势。

关键词 光学二次谐波产生, 反铁磁序, 空间反演对称性破缺, 相变, 物态调控



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光学二次谐波产生(second harmonic generation, SHG)是非线性光学的重要现象之一, 自20世纪60年代被发现以来^[1], 光学SHG技术经历了快速的发展, 在基础科学研究和实际应用中均取得了重大进展。在非线性光学理论研究方面, SHG效应的理论模型得到了重要扩展, 特别是在晶体材料中SHG过程的理论描述方

面, 晶体的对称性对SHG效率的影响规律被提出, 晶体中非线性极化张量的计算方法得到了系统发展^[2], 为后续研究者深入探索非线性效应奠定了理论基础。在非线性光学的实验研究方面, 近年来, SHG探测技术亦有了更广泛的应用, 尤其是利用光学SHG表征技术可以揭示被探测体系的空间反演对称性破缺、相变、极化

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耦合、铁电畴、铁电序演变和扭角相位匹配等^[3-27]。例如,利用光学SHG方法研究异质结界面和薄膜晶体结构的反演对称破缺^[11-23]、铁电性氧化物薄膜的铁电序演变^[24,25]、具有超高热电性能的 ClO_4 分子的结构对称性破缺^[26]和弛豫铁电薄膜中的极化耦合演变,并发现证实了具有超高储能密度的超顺电态^[27]等。研究人员还发现,光学SHG不仅是一种用于探测体系中铁电序的成熟技术,而且能够成熟地用于探测体系中长期难以表征的反铁磁序^[28-32]。

相较于铁磁体(ferromagnets, FM),反铁磁体(anti-ferromagnets, AFM)是一类具有长程磁性有序但净磁化强度为零的磁性体系^[33]。这种精确的磁矩抵消使得反铁磁体对外部磁场扰动不敏感,同时具有亚皮秒级的自旋动力学和对外部扰动的鲁棒性,这些特性使得反铁磁体在下一代信息技术中具有重要的应用潜力^[34]。例如,反铁磁性使其在磁存储器件中具有高稳定性和快速响应的优势^[34,35]。然而,由于缺乏宏观的磁化强度,传统的表征手段难以直接探测反铁磁体的内部磁性结构和动态过程^[36,37]。在磁性材料的研究中,理解磁性结构及其与晶体结构之间的耦合是基础物理研究和技术发展的关键问题之一。反铁磁体的磁性结构通常涉及复杂的自旋排列,这些自旋排列往往与晶格畸变和电子结构紧密相关^[33]。因此,发展能够直接探测和表征这些反铁磁性结构的技术对于推动反铁磁材料的基础研究和应用至关重要^[36]。目前有多种检测技术可用于探测大尺寸块状晶体中的反铁磁序,代表性的技术手段就是中子衍射。然而,对于构成器件构造模块的超薄外延薄膜的宏观物性以及超快瞬态过程或空间分辨检测,这种技术通常是不适用的。为了克服这一困难,科研人员发展了多种先进的表征技术,其中SHG技术因其高灵敏度、无损探测、环境适应能力强等优势脱颖而出,图1(a)为基于电磁辐射与反铁磁序相互作用的示意图。

光学SHG技术在表征反铁磁体系中具有显著的优势,尤其在中心反演对称性变化表征、高灵敏度表面表征、相变表征和物态调控的研究方面展现出独特性。相比于中子衍射技术,光学SHG技术的空间分辨率更高,且对薄膜和低维体系更为适用和高效便捷^[38,39];与磁光克尔效应(magneto-optical Kerr effect, MOKE)和拉曼散射相比,SHG对反演对称性破缺和某些磁电耦合体系更具有敏感性^[40];相较于扫描NV (nitrogen vacancy)磁力仪,SHG具备无损探测、抗环境干扰

能力强等优点^[41]。结合多外场(电场、磁场、温度场和应力场等)的调控手段,SHG是研究反铁磁体系和多铁性体系的重要工具,同时与其他技术互补,为全面研究反铁磁体的自旋排列、磁畴结构和相变等提供了更多维度的信息^[37]。SHG过程涉及两个相同频率光子的湮灭和一个双频率光子的产生,这一过程对于材料的对称性非常敏感,尤其是对于反铁磁体系中的磁畴结构和磁化过程^[42]。此外,SHG技术的空间分辨率可以达到亚微米级别,故通过偏振依赖的SHG显微成像技术可以研究反铁磁体的微观磁畴结构、磁畴壁和表面效应等。

在过去的近20年里,反铁磁体系SHG效应的理论研究和SHG技术用于反铁磁体系探测的实验研究都在逐步发展进步,研究的体系包括但不限于 Cr_2O_3 ^[43,44]、 NiO ^[45]、 BiFeO_3 ^[37]、 CrI_3 ^[29]、 NiI_2 ^[31]、 MnPS_3 ^[30]和 MnPSe_3 ^[32]等。这些研究不仅揭示了反铁磁体内部的磁性结构,还发现了磁电耦合导致的新奇现象。例如,电场调控的磁畴翻转和光脉冲在反铁磁体系中诱导的电子极化^[37,43],这些新奇的现象促使我们对相关理论和实验展开进一步的深入研究。本文将详细介绍光学SHG技术的基本原理、实验方法以及在反铁磁体研究中的应用。我们将讨论SHG如何帮助研究人员理解反铁磁体的磁畴结构、磁电耦合效应、反铁磁相变以及在外场作用下的动态响应。通过这些研究,我们可以更好地理解反铁磁体的物理性质,并探索其在新型信息存储和处理技术中的应用潜力。

1 光学SHG技术表征反铁磁体的原理概述

非线性光学现象在先进的光子学和电子设备中扮演着核心角色,因为它们控制着诸如转导和开关等功能,并导致不同自由度相互作用的非平凡物理现象^[46]。光学SHG是指在非线性介质中,输入激光束的光频率为 ω 的两个光子经由系统的虚拟能级上转换为光频率为 2ω 的单个光子^[47],如图1(b)所示。该过程可以表示为

$$P(2\omega = \omega + \omega) = \chi^{(2)} E(\omega)E(\omega), \quad (1)$$

式中, $E(\omega)$ 为入射光电场, $\chi^{(2)}$ 为二阶非线性光学极化率张量。在多极近似下, $\chi^{(2)}$ 可表示为

$$\chi^{(2)}(\omega, q) \approx \chi_{\text{ED}}^{(2)}(\omega) + \chi_{\text{EQ}}^{(3)}(\omega)q + o(q^2), \quad (2)$$

式中, $\chi_{\text{ED}}^{(2)}$ 和 $\chi_{\text{EQ}}^{(3)}$ 分别为电偶极子(electric dipole, ED)项和电四极子(electric quadrupole, EQ)项的贡献^[48]。对于

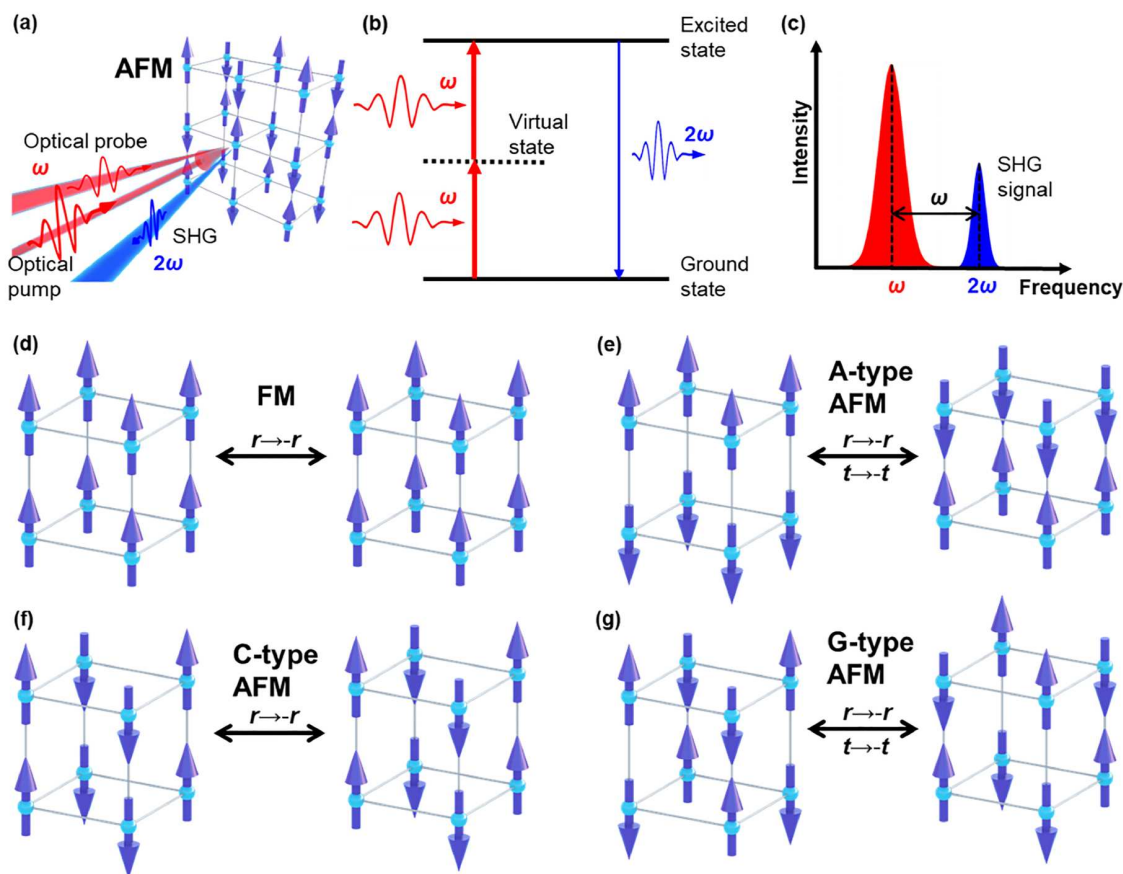


图1 (网络版彩色)光学SHG和反铁磁序. (a) 光学SHG探测反铁磁序示意图. (b) 光学SHG过程的能级示意图. (c) 光学SHG过程入射光和出射光的光谱位置. (d)~(g) 铁磁序、A型反铁磁序、C型反铁磁序和G型反铁磁序的自旋排列示意图

Figure 1 (Color online) Optical SHG and antiferromagnetic order. (a) Schematic diagram of optical SHG probing antiferromagnetic order. (b) Schematic diagram of the energy levels of the optical SHG process. (c) Spectral positions of input and output light in the optical SHG process. (d)~(g) Schematic diagrams of the spin arrangement of ferromagnetic order, A-type antiferromagnetic order, C-type antiferromagnetic order and G-type antiferromagnetic order, respectively

具有磁序的晶体材料, 其 $\chi^{(2)}$ 可表示为

$$\chi^{(2)} = \varepsilon_0(\chi^{(i)} + \chi^{(c)}), \quad (3)$$

其中, 时不变张量 $\chi^{(i)}$ 和时非不变张量 $\chi^{(c)}$ 分别表示晶体结构和磁序结构引起的对称性破缺^[37]. 一般倍频光(2ω)的强度会比入射光(ω)的强度弱一些, 并且在中心频率附近呈高斯分布, 如图1(c)所示. 光学SHG已被证明是一种探测复杂结构和磁序分布的强大技术, 能够有效探测到样品中晶体结构或者磁性结构引起的中心反演对称破缺^[29,30]. 这表明先进的光学SHG技术对于研究反铁磁体对外场调控的响应至关重要, 包括研究反铁磁畴壁的成核和其扩张的重要特性等^[37,49,50].

前面提到了对于晶格空间反演对称性破缺的系统, 光学SHG是存在电偶极子项的贡献的, 并且被称为时

间不变型(又称为i型过程). 在存在晶格反演对称性的情况下, 如果存在破坏空间反演和时间反演对称性的磁性结构, SHG也可以允许发生^[47,51], 这种电偶极子允许的SHG变为非时间不变型(又称为c型过程). 与i型SHG相比, c型SHG一般不太常见, 而且通常其信号会更弱. 当然, 并不是所有的磁性结构都会产生c型SHG信号^[29]. 如图1(d)所示是一个典型的铁磁序, 在考虑自旋的情况下作完空间反演($r \rightarrow -r$)操作后得到的仍然是其自身, 不存在由磁序带来的额外空间反演破缺. 因此在电偶极子近似下, 铁磁有序体系中的c型SHG是被禁止的(例如: 铁磁性 SrRuO_3).

另一方面, 对于最简单的一种反铁磁序(A型反铁磁, 如图1(e)所示), 其双层反铁磁结构的所有自旋都指向上或向下. 在考虑自旋的情况下作空间反演操作得

到的不是原来的结构, 必须在做完空间反演操作之后再作时间反演($t \rightarrow -t$)操作才能得到原来的结构. 因此, A型反铁磁序同时打破了时间反演和空间反演对称性, 从而允许电偶极子c型SHG产生(例如: 双层反铁磁性 CrI_3). 然而, 也不是所有的反铁磁序都会同时打破时间反演和空间反演对称性从而产生c型SHG信号^[30]. 如图1(f)为C型反铁磁序, 在考虑自旋的情况下对其作空间反演操作得到的仍然是其本身. 因此, 在电偶极子近似下C型反铁磁序中的c型SHG是被禁止的(例如: 二维反铁磁性 FePS_3). 而对于G型反铁磁序(如图1(g)所示, 典型的体系有 Cr_2O_3 和 BiFeO_3 等), 其作完空间反演操作之后必须再作时间反演操作才能得到其原来的结构, 因此G型反铁磁序也允许产生c型SHG信号. 可以发现, 对于反铁磁序, 必须是沿着自旋极化方向的层间反铁磁自旋方向相反, 其才会存在由反铁磁序带来的额外空间反演破缺从而允许c型SHG.

2 光学SHG技术在反铁磁性研究中的应用

光学SHG表征技术通过分析反射和透射SHG信号

的强度、微区域分布和偏振各向异性图案的变化, 可以提供反铁磁体中的磁有序信息. 因此, 光学SHG方法在反铁磁体系的研究中有着广泛的应用. 首先, 光学SHG方法能够直接观测到反铁磁材料中的反铁磁序(antiferromagnetic order, AF), 这对于理解层数依赖的磁性材料中的磁性行为至关重要. 如在 NiI_2 、 FePS_3 和 VPS_3 等材料中, SHG信号的变化与反铁磁序的建立和破坏直接相关^[52-54]; 其次, 亚微米级空间分辨率光学SHG显微成像技术(如图2(a)所示)可以用于图像化反铁磁材料中的反铁磁畴结构^[37]. 由于不同排布的反铁磁序带来的额外空间反演破缺的强弱和方向都有所不同, 因此对于拥有不同磁畴的一个区域而言, 其SHG的偏振各向异性强度和强度分布也会有所不同(如图2(b), (c)所示), 这对于理解反铁磁体系中的磁畴动力学和磁畴壁的行为至关重要^[55]; 此外, 通过测量反铁磁体系中SHG信号的温度依赖性, 可以研究反铁磁序随温度的演化并获得其Néel温度(T_N), 这对于理解反铁磁相变和磁性调控非常重要. 如图2(d)所示, BiFeO_3 (BFO)薄膜SHG信号的温度依赖性显示其Néel温度约为618 K^[28]. 并且,

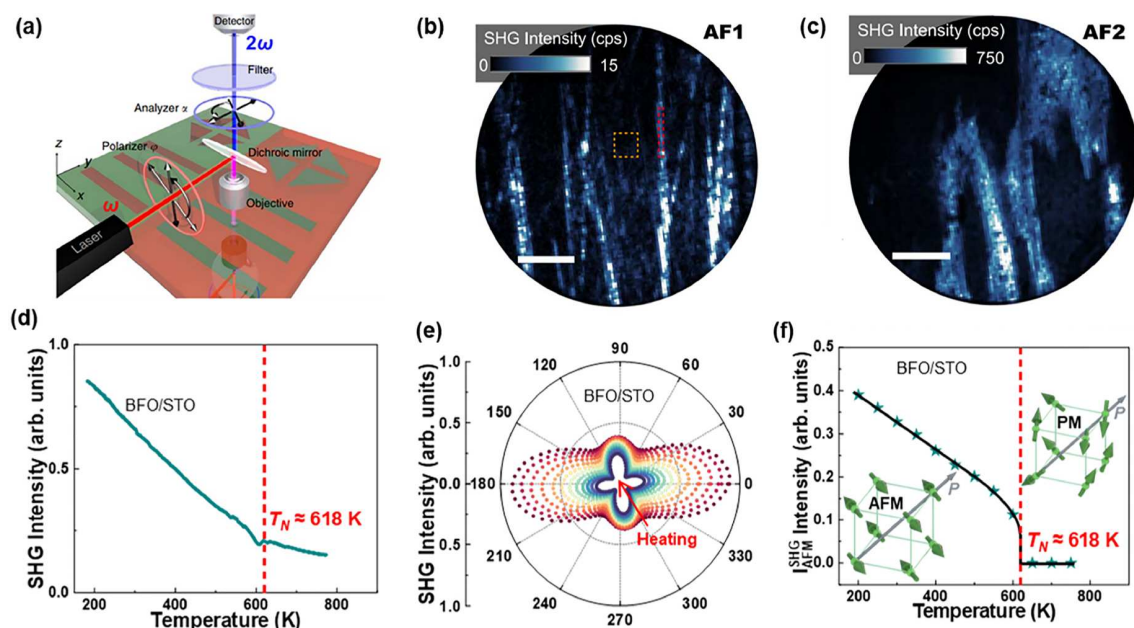


图 2 (网络版彩色)光学SHG表征技术探测反铁磁序和反铁磁相变. (a) 光学SHG显微成像技术的示意图^[7]. (b) 在非多铁性AF1相中获得的SHG mapping图像^[55]. (c) 在多铁性AF2相中获得的SHG mapping图像^[55]. (d) 在 p - p 偏振配置下BFO薄膜的SHG强度随温度的变化^[28]. (e) BFO薄膜在不同温度下测量得到的偏振各向异性图案^[28]. (f) 从图(e)中提取的反铁磁序贡献的温度依赖的SHG信号^[28]

Figure 2 (Color online) Probing antiferromagnetic order and antiferromagnetic phase transition by optical SHG characterization technique. (a) Schematic diagram of optical SHG microscopy^[7]. (b) SHG mapping image obtained in the non-multiferroic AF1 phase^[55]. (c) SHG mapping image obtained in the multiferroic AF2 phase^[55]. (d) The SHG intensity of BFO films as a function of temperature in the p - p polarization configuration^[28]. (e) Polarization anisotropy patterns of BFO films measured at different temperatures^[28]. (f) Temperature dependent SHG signals contributed by antiferromagnetic order extracted from (e)^[28]

由于多铁体中的铁电序和反铁磁序同时对SHG信号有贡献, 光学SHG方法还可以用于研究多铁体中的磁电耦合效应。如图2(e)所示, 多铁性体系(如BFO薄膜)的偏振各向异性图案与传统单一铁电体系或反铁磁体系是不一样的, 它是非对称的^[28]。通过拟合分析, 可以从不同温度下的偏振各向异性图案中提取铁电序和反铁磁序的贡献。图2(f)为拟合提取得到的反铁磁序贡献的SHG信号的温度依赖性, 通过对其拟合分析得到的反铁磁-顺磁相变温度与图2(d)中信号转折的温度点一致, 这进一步佐证了光学SHG方法表征反铁磁相变的准确性和有效性^[28]。

最后, 因为某些反铁磁体系中的反铁磁序会通过自旋-轨道耦合(spin-orbital coupling, SOC)将低的磁对称性投射到晶格上并引起小的极化位移, 可以破坏体系的空间反演对称性^[56], 而SHG信号可以敏感地反映出这些微小的对称性变化^[28], 所以通过测量SHG信号强度随外场(如: 应力场、电场、磁场和温度场等)调控的变化, 可以定量地研究外场对反铁磁序的自旋排列调控和影响, 从而为研究自旋相关的效应提供了重要

手段。从非线性光学效应的角度考虑, SOC破坏空间反演对称性会引入新的二阶非线性极化率张量的分量或增加现有的分量, 改变SHG信号的强度、偏振依赖性和外场依赖特性。通过多外场可调的偏振各向异性SHG和SHG光谱强度测量, 可解析量化SOC对反铁磁体系中空间反演对称性破缺的具体影响。

3 总结

光学二次谐波产生表征技术为反铁磁体系的研究提供了全新的视角和强有力的技术支持。通过对反铁磁体系的二阶非线性光学特性进行深入研究和探讨, 研究人员能够全面理解某些(低维)反铁磁体系的自旋排列、相变机制、外场依赖特性、空间反演对称性特征和磁电耦合效应等, 这对于理解低维磁性和开发新型磁电器件具有重要的指导意义。未来, 随着科学技术的进一步发展, 先进的光学二次谐波产生表征技术有望在反铁磁体系及其他相关体系的研究中进一步发挥更加重要的作用, 进一步推动相关领域研究的进步和发展。

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Summary for “利用光学二次谐波产生表征技术研究反铁磁体”

Antiferromagnets studied by optical second harmonic generation characterization techniques

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Antiferromagnets have garnered significant attention due to their unique magnetic properties and promising application prospects in the fields of information storage, spintronics, and quantum computing. Unlike ferromagnetic materials, where the magnetic moments of adjacent atoms align parallel, antiferromagnetic materials exhibit an antiparallel alignment of adjacent spins. This results in a net magnetic moment of zero in an ideal case and a property that eliminates stray magnetic fields, offering advantages for high-density magnetic storage and spintronic devices. However, the lack of a nonzero net magnetic moment also makes the detecting and characterizing of the antiferromagnetic order exceptionally challenging using conventional techniques. The search for effective methods to probe the intricate properties of antiferromagnetic materials has thus become a critical topic of modern physics. Optical second harmonic generation (SHG) has emerged as a powerful tool for characterizing antiferromagnetic materials. As a nonlinear optical process, SHG involves two photons combining into one with twice the photon frequency, which is a phenomenon sensitive to asymmetry properties such as spatial inversion symmetry breaking. This sensitivity makes SHG ideal for studying small-scale or delicate materials, including thin films and two-dimensional (2D) systems, positioning it as a key method for investigating antiferromagnetic properties and dynamics. One primary application of SHG is characterizing spatial inversion symmetry breaking induced by antiferromagnetic order. Polarization-dependent SHG signals provide insights into both the material symmetry and the spin configurations. This is particularly useful for materials like chromium oxide and bismuth ferrite, which exhibit intricate antiferromagnetic structures. SHG also excels in probing spin dynamics and phase transitions. By tracking the variation of symmetry and spin structures during phase transitions, such as from paramagnetic to antiferromagnetic, SHG can reveal the phase transition temperatures and mechanisms. Time-resolved SHG experiments can monitor ultrafast spin dynamics with femtosecond resolution, capturing real-time evolution under external perturbations. Another significant application is visualizing magnetic domain structures and magnetoelectric coupling effects. Conventional methods struggle to detect antiferromagnetic domains due to their zero net magnetic moment, but the sensitivity of SHG to local symmetry allows detailed antiferromagnetic domain imaging. For instance, SHG microscopy has mapped magnetic domains in bismuth ferrite thin films, revealing domain configurations and their responses to electric or magnetic fields—Insights crucial for optimizing multiferroic materials. The exploration of 2D antiferromagnetic materials, such as CrI₃ and MnPS₃, further underscores the versatility of SHG technology. These materials exhibit unique magnetic behaviors and strong spin-lattice coupling due to reduced dimensionality. SHG has identified their distinctive properties, including phase transitions and responses to external fields like magnetic and optical excitation. In summary, SHG technology offers a versatile and sensitive approach for studying antiferromagnetic materials. Due to its ability to probe spatial inversion symmetry breaking, spin dynamics, phase transitions, and magnetic domain structures, SHG has become an indispensable tool for unraveling the complexity of antiferromagnetic order. Future advancements in SHG experimental techniques, such as higher spatial and temporal resolution and the integration with complementary methods, are expected to further enrich its applications. As researchers continue uncovering the micro-mechanisms of antiferromagnetism, SHG will play a pivotal role in advancing both fundamental understanding and technological applications in this exciting field.

optical second harmonic generation, antiferromagnetic order, spatial inversion symmetry breaking, phase transition, manipulation of physical properties

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