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Giant anisotropic nonlinear optical response in transition metal monopnictide Weyl semimetals

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A. Dependence of SHG amplitude on polarization for different crystal and surfaces used in this study

In general, the polarization, $\mathbf{P}$, in materials has contributions from higher orders of the electric field, $\mathbf{E}$, in addition to the linear response, such that,

$$\mathbf{P} = \mathbf{P_0} + \epsilon_0 \chi_e \mathbf{E} + \epsilon_0 \chi^{(2)} \mathbf{E}^2 + \cdots \tag{1}$$

In noncentrosymmetric materials the second order term, $P_i^{(2)} = \epsilon_0 \chi_{ijk} E_j E_k$, that gives rise to frequency mixing, SHG, and optical rectification, is allowed[1, 2]. The latter two phenomena arise from excitation with a single frequency, such that there is an automatic symmetry with respect to permutation of the second and third indices. This motivates the use of a 3×6 second rank tenor d_{ij} instead of χ_{ijk}[1]. The relation between d_{ij} and χ_{ijk} is as follows: the first index $i = 1, 2, 3$ in d_{ij} corresponds to $i' = x, y, z$ respectively in $\chi_{i'j'k'}$ and the second index $j = 1, 2, 3, 4, 5, 6$ in d_{ij} corresponds to $j'k' = xx, yy, zz, yz/zy, zx/xz, xy/yx$ in $\chi_{i'j'k'}$[1]. In terms of the d tensor, the relation between second order polarization and electric field has the form[1]:

$$\begin{bmatrix} P_1(2\omega) \\ P_2(2\omega) \\ P_3(2\omega) \end{bmatrix} = 2\epsilon_0 \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \begin{bmatrix} E_1^2(\omega) \\ E_2^2(\omega) \\ E_3^3(\omega) \\ 2E_2(\omega)E_3(\omega) \\ 2E_1(\omega)E_3(\omega) \\ 2E_1(\omega)E_2(\omega) \end{bmatrix}. \tag{2}$$

For a crystal with effective point group symmetry $4mm$, the nonzero elements are $d_{15} = d_{24}$, $d_{31} = d_{32}$ and d_{33}. Note that transition metal monopnictides (TMMPs) such as TaAs belong to the non-symmorphic $I4_1md$ space group which has screw rotation instead of C_4 rotation. However, screw and C_4 rotation symmetries lead to the same constraints on $\chi^{(2)}$ in optics and therefore SHG is described by the $4mm$ point group in TMMPs. Predictions based on Eq. 2 for the angular dependence of the SHG intensity for four scans that involve linear polarized light normally incident on the TaAs or TaP or NbAs (112) surface are given below. Eqs. 3 and 4 refer to scans where two polarizers are synchronously rotated to simulate rotation of the sample. Note that we omitted the constant of $2\epsilon_0$ in the following calculations. I_{para} and I_{perp} correspond to generator and analyzer polarization set parallel and perpendicular, respectively,

$$I_{para}(\theta_1) = \frac{1}{27}|(d_{33} + 4d_{15} + 2d_{31})\cos^3\theta_1 + 3(2d_{15} + d_{31})\sin^2\theta_1 \cos\theta_1|^2, \tag{3}$$

$$I_{perp}(\theta_1) = \frac{1}{27}|(d_{33} - 2d_{15} + 2d_{31})\cos^2\theta_1 \sin\theta_1 + 3d_{31}\sin^3\theta_1|^2. \tag{4}$$

Eqs. 5 and 6 refer to scans where the analyzer is fixed at 0° (parallel to [1,1-1] crystal axis) and 90° (parallel to [1,-1,0] crystal axis), respectively, and the direction of linear polarization of the generator is scanned,

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$$I_{0^\circ}(\theta_1) = \frac{1}{27}|(d_{33} + 4d_{15} + 2d_{31})\cos^2\theta_1 + 3d_{31}\sin^2\theta_1|^2, \tag{5}$$

$$I_{90^\circ}(\theta_1) = \frac{1}{3}|d_{15}|^2\sin^2(2\theta_1). \tag{6}$$

The remaining scan that provides independent information constraining the elements of the d tensor is a measurement of SHG circular dichroism, which is the difference in SHG intensity with incident light of left and right circular polarization. To lowest order in d_{ij},

$$I_{\sigma^+}(\theta_2) - I_{\sigma^-}(\theta_2) = \frac{2}{9}\mathrm{Im}\{d_{15}d_{33}^*\}\sin 2\theta_2. \tag{7}$$

The circular dichroism in SHG is proportional to $Im(d_{33}d_{15}^*)$ and therefore measures the component of d_{15} that is out-of-phase with d_{33}. From comparison of the circular dichroism and linear polarization measurements we find a relative phase of 30 ° (± 10 °) between d_{15} and d_{33} at 300 K.

The benchmark materials, GaAs and ZnTe, have the same point group $\bar{4}3m$, and the only nonzero components of the d tensor are $d_{14} = d_{25} = d_{36}$. For light normally incident on the ZnTe (110) surface, the SHG angular dependencies are:

$$I_{para}(\theta_1) = 9|d_{14}|^2\cos^4\theta_1\sin^2\theta_1, \tag{8}$$

$$I_{perp}(\theta_1) = |d_{14}|^2(2\cos\theta_1\sin^2\theta_1 - \cos^3\theta_1)^2. \tag{9}$$

For GaAs (111) they are:

$$I_{para}(\theta_1) = \frac{2}{3}|d_{14}|^2(cos^3\theta_1 - 3\cos\theta_1\sin^2\theta_1)^2. \tag{10}$$

$$I_{perp}(\theta_1) = \frac{2}{3}|d_{14}|^2(\sin^3\theta_1 - 3\cos^2\theta_1\sin\theta_1)^2. \tag{11}$$

B. Obtaining nonlinear response coefficients from benchmark materials

From Eq. 3, the peak SHG intensity from TaAs (112) is proportional to $|d_{\mathrm{eff}}|^2/27$, where $d_{\mathrm{eff}} \equiv d_{33} + 4d_{15} + 2d_{31}$. Peak SHG intensities from ZnTe (110) and GaAs (111) are proportional to $4|d_{14}|^2/3$ and $2|d_{14}|^2/3$, respectively. When measured in reflection, in addition to the nonlinear response coefficients, the SHG intensity depends on the index of refraction at the fundamental and the second harmonic frequencies. To compare SHG intensities from different compounds we use a formula derived by Bloembergen and Pershan [3],

$$\chi_R^{(2)} \equiv -\frac{E_R(2\omega)}{\epsilon_0 E(\omega)^2} = \frac{\chi^{(2)}}{(\epsilon^{1/2}(2\omega) + \epsilon^{1/2}(\omega))(\epsilon^{1/2}(2\omega) + 1)}T(\omega)^2. \tag{12}$$

where ϵ is the relative dielectric constant, 'R' stands for reflection geometry and $T(\omega) = \frac{2}{n(\omega)+1}$ is the Fresnel coefficient of the fundamental light. Values for index of refraction were taken from the literature: ZnTe[4], GaAs[5] and complex index of TaAs was measured by the method that can be found in Ref. 6. The correction factor turns out to be small, less than 20%, because the indices of refraction for the three compounds are similar in magnitude (within 30 % difference) at the relevant frequencies. Without taking account of this correction, we obtain $|d_{33}| \sim 3000 \pm 450$ pV/m for TaAs by referring to the value of ZnTe[7].

After establishing the relative size of the d coefficients by the procedure described above, we used measurements of the absolute amplitude of d_{14} in ZnTe *et al.*[7] to obtain absolute amplitudes for GaAs and TaAs. As reported in

the main text, we obtain $|d_{33}| \sim 3600$ pV/m in TaAs. Using the same procedure of referencing to ZnTe, we obtain $|d_{14}| \sim 380$ pV/m for GaAs, which agrees with the literature value[8].

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