

Spectroscopic ellipsometry study of optical anisotropy in $\text{Gd}_5\text{Si}_2\text{Ge}_2$ and comparison with reflectance difference spectra

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The complex dielectric functions of single crystals of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ were obtained using spectroscopic ellipsometry (SE) in the photon energy range of 1.5–5.0 eV at room temperature. Reflectance difference (RD) spectra for the a - b and b - c planes of single crystals of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ were derived from these dielectric functions and compared to those obtained from reflectance difference spectroscopy (RDS) at near-normal incidence. The two experimental RD spectra from SE and RDS agreed well. The in-plane optical anisotropy of the sample is mainly due to intrinsic bulk properties because of its larger magnitude (4×10^{-2}) compared to surface-induced optical anisotropies, with a magnitude of only about 10^{-3} for a typical cubic material.

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I. INTRODUCTION

Recently, $\text{Gd}_5\text{Si}_2\text{Ge}_2$ has been extensively studied due to its giant magnetocaloric effect, colossal magnetostriction, and giant magnetoresistance in the region of an unusual first-order magnetic-structural phase transformation.^{1–3} It is currently being considered as a promising magnetic regenerator material for active refrigeration.² At room temperature, it has a monoclinic structure (P112₁/a) with lattice constants $a = 7.5891$, $b = 14.827$, and $c = 7.7862$ Å and an angle (γ) of 93° between the a and b axes.³ There have been various studies of thermal, electronic, and magnetic properties of this material,^{4,5} but little work on the optical properties. Recently, angle-dependent reflectance-difference (ARD) spectra for $\text{Gd}_5\text{Si}_2\text{Ge}_2$ single crystals have been measured by rotating differently oriented specimens.⁶ The reflectance difference (RD), defined as $\Delta R/R$, the ratio of the difference divided by the average of two orthogonal reflectances, could be obtained from the largest values of the ARD spectra.⁷ The reflectance of a cubic material from ambient (air) at normal incidence can be obtained easily with $R = |(1 - \sqrt{\epsilon}) / (1 + \sqrt{\epsilon})|^2$ from the complex dielectric constants. The dielectric constant of a cubic material is a scalar quantity. It becomes a 3×3 tensor for an anisotropic material. The RD spectrum gives relative reflectance differences in the reflection plane, not absolute values. To fully understand optical properties of anisotropic materials, absolute values of the dielectric tensor components are required. From the dielectric tensor components of an anisotropic material, measured by spectroscopic ellipsometry, we can get reflectances for light polarized in any direction and can compare the RD spectra to those obtained with ARD.

RD arises from intrinsic bulk or surface effects. Bulk RD anisotropy originates from a nonorthogonal lattice or unequal lengths of the lattice parameters, whereas surface anisotropy

is from symmetry breaking on the surface.⁸ The reflected plane-polarized light is related to the incident s -polarized (electric field perpendicular to the plane of incidence) and p -polarized (electric field parallel to the plane of incidence) fields at nonzero incidence angle via a 2×2 reflection-coefficient matrix,

$$\begin{bmatrix} E_s \\ E_p \end{bmatrix}_{\text{out}} = \begin{pmatrix} r_{ss} & r_{sp} \\ r_{ps} & r_{pp} \end{pmatrix} \begin{bmatrix} E_s \\ E_p \end{bmatrix}_{\text{in}}. \quad (1)$$

The reflection-coefficient matrix for isotropic materials does not have off-diagonal components. The room-temperature monoclinic structure of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ has a deviation of about 3° from the orthogonal, compared to the low-temperature orthorhombic structure. Therefore, small off-diagonal reflection coefficients, r_{sp} and r_{ps} , are expected in the monoclinic structure of $\text{Gd}_5\text{Si}_2\text{Ge}_2$. Theoretical calculations have been made for electronic, structural, optical, and magneto-optical properties of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ with the local spin-density approximation (LSDA).^{9,10} Validation of these theoretical calculations can be achieved from the comparison with experimental optical and RD spectra.

Optically anisotropic materials have two (for uniaxial crystals) or three (for biaxial crystals) different diagonal components of the dielectric tensor.¹² Using spectroscopic ellipsometry, the real and imaginary parts of the complex dielectric constants as a function of wavelength can be determined.¹³ Generalized ellipsometry is required for investigating optical properties of anisotropic materials that do not have orthogonal principal axes.¹⁴ To get complete sets of dielectric functions of anisotropic materials, additional measurements with sample surfaces of different crystal orientations or with different incidence angles are required. Instead of changing the experimental setup, the in-plane dielectric functions can be obtained by simply rotating the sample

about the surface normal. If there is no magneto-optic effect, materials having orthogonal principal axes do not have finite values of r_{sp} , r_{ps} . When the dielectric functions are slightly different, two in-plane orthogonal dielectric functions could be obtained from the ellipsometry measurements by rotating the sample by 90° .

II. EXPERIMENT

$\text{Gd}_5\text{Si}_2\text{Ge}_2$ single crystals were grown as in Ref. 11. Appropriate quantities of high-purity gadolinium (99.996%), prepared by the Materials Preparation Center of the Ames Laboratory; silicon (99.9999%); and germanium (99.999%) were arc melted several times under an argon atmosphere. The arc-melted button was then used as the charge material in a tri-arc crystal-pulling unit. A tungsten rod was used as the seed material that resulted in a randomly oriented $\text{Gd}_5\text{Si}_2\text{Ge}_2$ crystal. The as-grown crystal was oriented by back-reflection Laue diffraction and the crystallographic directions assigned using x-ray diffraction 2θ scans. The two oriented single crystals, a axis and c axis perpendicular to the surface, were cut by spark erosion, and the oriented faces were ground flat using standard metallographic techniques. The samples were polished with 3, 1, and $0.3 \mu\text{m}$ Al_2O_3 powder for optical measurements. The optical properties of the samples after polishing, therefore, may be slightly different when compared to an “ideal” surface unaffected by mechanical polishing.

The RD spectra were measured using the same method employed in Ref. 6. ARD of a $\text{Gd}_5\text{Si}_2\text{Ge}_2$ crystal has an angle dependence, $\sin(2\theta)$, where θ is the angle between the crystallographic axis and the incident linear polarization. RD spectra can be obtained from the maximum values of ARD when θ is 45° . Measured RD spectra in this work have the same shapes, but slightly smaller magnitudes compared to previous measurements, about 90% of that reported in Ref. 6, due to slightly different sample compositions and surface treatments.

We assumed that the crystal has three different dielectric functions and ignored the off-diagonal components of the dielectric tensor, i.e., there are no r_{sp} , r_{ps} terms in the reflection coefficient matrix because γ deviates only 3° from 90° . The spectroscopic ellipsometry (SE) was performed in the photon-energy range of 1.5–5.0 eV at room temperature with a 68° angle of incidence and no applied magnetic field. Ellipsometry measures the complex dielectric function of the sample from the complex ratio of the complex reflection coefficients for s - and p -polarized light. In this paper, we report dielectric functions of anisotropic $\text{Gd}_5\text{Si}_2\text{Ge}_2$ crystals measured with SE and comparison with the data with RD spectra.

The complex pseudodielectric functions can be obtained from the Fresnel equations for an anisotropic material.^{13,15} The complex reflectance ratio $\rho e^{i\Delta} = r_{pp}/r_{ss}$ of p - and s -polarization is

$$\rho e^{i\Delta} = \left(\frac{\sqrt{\varepsilon_c - \sin^2 \phi} - \sqrt{\varepsilon_a \varepsilon_c} \cos \phi}{\sqrt{\varepsilon_c - \sin^2 \phi} + \sqrt{\varepsilon_a \varepsilon_c} \cos \phi} \right) \left(\frac{\cos \phi + \sqrt{\varepsilon_b - \sin^2 \phi}}{\cos \phi - \sqrt{\varepsilon_b - \sin^2 \phi}} \right), \quad (2)$$

where ϕ is the angle of incidence, and ε_a , ε_b , and ε_c are the complex pseudodielectric functions along the a , b , and c

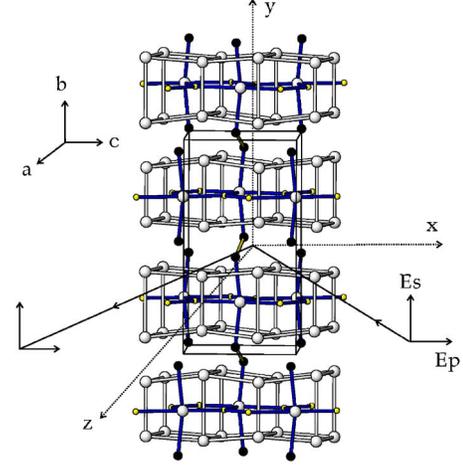


FIG. 1. (Color online) Experimental configuration for a -axis $\text{Gd}_5\text{Si}_2\text{Ge}_2$ with the b axis pointing in the y direction. The plane of incidence is the x - z plane, and the z direction is normal to the sample surface. Large spheres are Gd atoms, and small ones are Si or Ge atoms.

axes, respectively, for the orientation denoted by $axbycz$ as in Ref. 15. Rotating-analyzer ellipsometry (RAE) measures the complex reflectance ratio r_{pp}/r_{ss} with Fourier analysis, and the real and imaginary parts of $\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2$ can be then obtained, simultaneously, from the following relations without using the Kramers-Kronig relations:

$$\varepsilon = \sin^2 \phi + \sin^2 \phi \tan^2 \phi \left(\frac{1 - \rho e^{i\Delta}}{1 + \rho e^{i\Delta}} \right)^2. \quad (3)$$

$\rho e^{i\Delta}$ has the same value at any orientation of an optically isotropic material. In the anisotropic case, it depends on the sample orientation.

Figure 1 represents the configuration of an a -axis sample (having a b - c plane surface) oriented with the b axis along the s -polarization direction (y direction). Equation (2) can be expressed for the orientation $cxbyaz$ as

$$\begin{aligned} \varepsilon_c &= \left(\frac{\varepsilon_a - \sin^2 \phi}{\varepsilon_a \cos^2 \phi} \right) \left(\frac{\Phi_b \cos \phi + \sqrt{\varepsilon_b - \sin^2 \phi}}{\cos \phi + \Phi_b \sqrt{\varepsilon_b - \sin^2 \phi}} \right)^2 \\ &= f_1(\varepsilon_a) f_2(\varepsilon_b), \end{aligned} \quad (4)$$

where $\Phi_b = (1 - \rho e^{i\Delta}) / (1 + \rho e^{i\Delta})$ is directly measurable from RAE with the b axis parallel to the s -polarization direction. If we rotate the sample by 90° around the z direction ($bxcyaz$ orientation), then b and c are switched and

$$\begin{aligned} \varepsilon_b &= \left(\frac{\varepsilon_a - \sin^2 \phi}{\varepsilon_a \cos^2 \phi} \right) \left(\frac{\Phi_c \cos \phi + \sqrt{\varepsilon_c - \sin^2 \phi}}{\cos \phi + \Phi_c \sqrt{\varepsilon_c - \sin^2 \phi}} \right)^2 \\ &= f_1(\varepsilon_a) f_2(\varepsilon_c). \end{aligned} \quad (5)$$

When $\varepsilon_{a,b,c} = \langle \varepsilon \rangle + \delta \varepsilon_{a,b,c}$ deviates from the average dielectric function $\langle \varepsilon \rangle$, the measured dielectric function ε with the orientation $cxbyaz$ can be expressed as¹⁶

$$\varepsilon = \langle \varepsilon \rangle + \frac{\langle \varepsilon \rangle - \sin^2 \phi}{(\langle \varepsilon \rangle - 1) \sin^2 \phi} \delta \varepsilon_c + \frac{\langle \varepsilon \rangle \cos^2 \phi - \sin^2 \phi}{(\langle \varepsilon \rangle - 1) \sin^2 \phi} \delta \varepsilon_b + \frac{1}{1 - \langle \varepsilon \rangle} \delta \varepsilon_a. \quad (6)$$

From the previously measured RD spectra from Ref. 6, the reflectances differ about 4% from the average. The differences among the three dielectric functions are small, and we can use Eq. (6). Therefore the z -component (normal direction) dielectric function is less important than the in-plane ones in the ellipsometry measurement if the average $\langle \varepsilon \rangle$ is >1 . With these assumptions, we can get the dielectric functions of the b and c components by an iterative method,

$$\varepsilon'_b = \varepsilon_c \frac{f_2(\varepsilon_c)}{f_2(\varepsilon_b)} = \varepsilon_c \left(\frac{\Phi_c \cos \phi + \sqrt{\varepsilon_c - \sin^2 \phi}}{\cos \phi + \Phi_c \sqrt{\varepsilon_c - \sin^2 \phi}} \right)^2 \times \left(\frac{\cos \phi + \Phi_c \sqrt{\varepsilon_c - \sin^2 \phi}}{\Phi_c \cos \phi + \sqrt{\varepsilon_c - \sin^2 \phi}} \right)^2, \quad (7)$$

$$\varepsilon'_c = \varepsilon_b \frac{f_2(\varepsilon_b)}{f_2(\varepsilon_c)} = \varepsilon_b \left(\frac{\Phi_b \cos \phi + \sqrt{\varepsilon_b - \sin^2 \phi}}{\cos \phi + \Phi_b \sqrt{\varepsilon_b - \sin^2 \phi}} \right)^2 \times \left(\frac{\cos \phi + \Phi_b \sqrt{\varepsilon_b - \sin^2 \phi}}{\Phi_b \cos \phi + \sqrt{\varepsilon_b - \sin^2 \phi}} \right)^2$$

where $\Phi_{b,c}$ are measured with RAE with the b and c axis pointing in the y direction. When the difference between two successive iterations was small enough ($\leq 10^{-5}$), the dielectric functions were considered to have converged. To make them converge, the choices of initial values of $\varepsilon_{b,c}$ are very important. Because the dielectric constant of the x -direction (intersection between the plane of incidence and the sample surface) is dominant,¹⁶ we used the initial ε_c and ε_b values from the SE measurement assuming they are cubic materials with the $cxbyaz$ and $bxcyaz$ orientations, respectively. The same procedure was applied to the c -axis sample to get ε_a and ε_b . The reflectivities for s - and p -polarizations are the same at normal incidence for cubic-symmetry materials. They become different at non-normal incidence. The difference is largest at about 70° and converges to 0 at 90° incidence angle. For anisotropic materials, there is a reflectivity difference between s - and p -polarizations even at normal incidence. The converged dielectric functions and initial values are not much different.

III. RESULTS AND DISCUSSION

Figure 2 shows the real parts of the dielectric functions for a -axis and c -axis surfaces of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ determined from ellipsometry by rotating the oriented single crystals. Dielectric functions of the b - c plane were measured for the a -axis crystal and those of the a - b plane were measured for the c -axis crystal. The measured real parts of ε_b from two different surfaces decrease as the photon energy increases, and the difference between them is <0.5 . Figure 3 is the measured imaginary part of the complex dielectric functions. The differences of the imaginary parts are larger than for the real

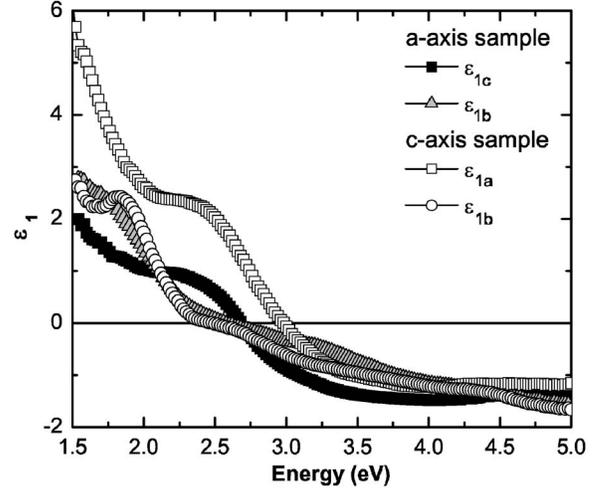


FIG. 2. The real part of the complex dielectric functions of the a - b and b - c planes of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ measured with ellipsometry.

ones because the crystal is a highly absorbing material at these frequencies and has large imaginary parts of the dielectric functions compared to the real parts. The differences between the two spectra of ε_b are most likely due to surface stress caused by the mechanical polishing process for optical measurements, slightly different compositions, and, possibly, different oxidation on the two inequivalent surfaces. The dielectric functions measured with the sample just after polishing and 24 h later have the same spectra. RD spectra are also reproducible over a few weeks. If there is oxidation, it occurs quickly and then stays stable or grows very slowly over a few weeks. The low-energy parts of the dielectric-function spectra are determined by interband transitions because the free-carrier (intraband, Drude) dielectric functions have smooth curves with $\varepsilon_1 < 0$, $d\varepsilon_1/d\omega > 0$ and $\varepsilon_2 > 0$, $d\varepsilon_2/d\omega < 0$. In the calculated dielectric functions,¹⁰ the Drude term appears at photon energies lower than 1.0 eV, which is out of our measurement range.

Figure 4 is the RD spectra of the b - c plane (a axis) and a - b plane (c axis) $\text{Gd}_5\text{Si}_2\text{Ge}_2$ measured from the ARD ro-

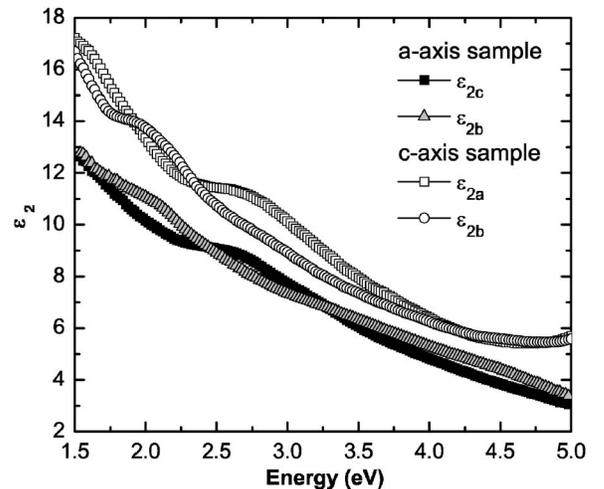


FIG. 3. The imaginary part of the complex dielectric functions of the a - b and b - c planes of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ measured with ellipsometry.

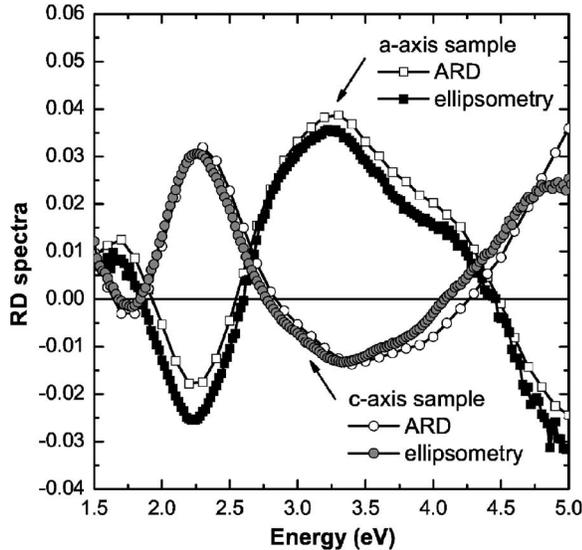


FIG. 4. RD spectra of the b - c plane and a - b plane $\text{Gd}_5\text{Si}_2\text{Ge}_2$. The spectra from the ellipsometry were scaled with 45% for the a axis (b - c plane) and 50% for the c axis (a - b plane) sample.

tated 45° from the incident polarization direction, and measured by ellipsometry. The b - c plane RD spectrum from ellipsometry was scaled down by 45% for the comparison. The spectrum has a negative peak at 2.2 eV and a positive peak at 3.2 eV. The zero-crossing lines and peak positions from different experiments agree well. The a - b plane RD spectra of the c -axis $\text{Gd}_5\text{Si}_2\text{Ge}_2$ measured from the ARD and from ellipsometry, scaled by 50%, show similar behavior. The overall amplitude differences of two measurements (scaled 45% for the b - c plane sample and 50% for the a - b plane sample) are mainly due to different angles of incidence. The normal incidence r_s and r_p values, measured at oblique incidence, deviate more than that measured at normal incidence. Since the structure of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ (Fig. 1) shows that the arrangement of atoms and their spacings along the a and c axes are similar, and different from those along the b axis, one expects the dielectric functions ϵ_{2a} and ϵ_{2c} to be similar, and different from ϵ_{2b} , in accord with the measured spectra.

Previous x-ray-induced photoelectron spectra from $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys showed that the Gd $4f$ electrons are located about 8 eV below the Fermi energy, and Gd $5d$ -Si(Ge) s - p covalently bonded states (or bands) are located about 2 eV below the Fermi energy.^{17,18} The states centered about 0.5 eV below the Fermi energy are due to Gd-Gd bonds or Gd $5d$ bands. From a comparison with the measured optical conductivity of Gd,^{19,20} the low-energy (~ 2 eV) optical transitions are primarily from Si(Ge) $3p(4p)$ -based bands to bands based on Gd $5d$ states. Any Gd d -to- f transitions should begin at 4 or 5 eV, if the unoccupied f states are 2–3 eV above the Fermi level. Transitions from the occupied $4f$ levels should begin at energies much higher than the upper limit of our spectra.

The interband contribution to the dielectric function of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ has been calculated,¹⁰ using electric-dipole matrix elements. It was averaged over all directions and broadened by convolution with a Lorentzian of 0.4 eV width. Figure 5

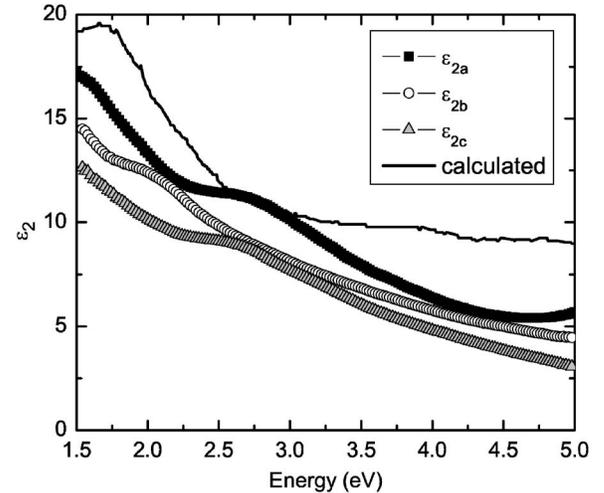


FIG. 5. Comparison of measured imaginary parts of the dielectric functions with angle-averaged spectrum from Ref. 10. The average values of the b - c and a - b planes were used for ϵ_{2b} .

shows the calculated ϵ_2 spectrum along with the measured ones. First we note that the magnitudes of calculated and measured spectra agree well. The most prominent structure in the calculated spectrum is a peak at ~ 1.75 eV, which may be identified with the weak peak at 2 eV in the ϵ_{2b} spectrum. However, if we were to average all three measured spectra, this peak would appear much weaker. The broad peak around 2.7 eV in ϵ_{2a} and ϵ_{2c} do not have a counterpart in the calculated spectrum. Finally, the calculated spectrum has broad weak structures around 3.5 and 4.8 eV, structures not definitively found in the measured spectra. (The rise in ϵ_{2a} above 4.5 eV may be an experimental artifact due to low detected light levels.)

IV. CONCLUSION

In summary, we measured the in-plane dielectric functions of anisotropic material $\text{Gd}_5\text{Si}_2\text{Ge}_2$ by ellipsometry. RD spectra obtained from the measured dielectric functions agreed well with RD spectra at normal incidence. From the agreement of two RD spectra, the dielectric functions of the anisotropic material can be obtained by iteration method and $\gamma=93^\circ$ in the monoclinic structure can be regarded as 90° . Two orthogonal measurements are sufficient to get the complex dielectric functions by choosing the specific orientation of the sample. The magnitudes of the measured dielectric-function spectra agree with that of the calculated angle-averaged spectrum, and there is partial agreement on the weak structures.

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- ¹V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).
- ²V. K. Pecharsky and K. A. Gschneidner, Jr., Appl. Phys. Lett. **70**, 3299 (1997).
- ³W. Choe, V. K. Pecharsky, A. O. Pecharsky, K. A. Gschneidner, Jr., V. G. Young, and G. J. Miller, Phys. Rev. Lett. **84**, 4617 (2000).
- ⁴E. M. Levin, A. O. Pecharsky, V. K. Pecharsky, and K. A. Gschneidner, Jr., Phys. Rev. B **63**, 064426 (2001).
- ⁵S. Yu. Dan'kov, A. M. Tishin, V. K. Pecharsky, and K. A. Gschneidner, Jr., Phys. Rev. B **57**, 3478 (1998).
- ⁶S. J. Lee, J. M. Park, J. E. Snyder, D. C. Jiles, D. L. Schlagel, T. A. Lograsso, A. O. Pecharsky, and D. W. Lynch, Appl. Phys. Lett. **84**, 1865 (2004).
- ⁷Z. Sobiesierski, D. I. Westwood, and C. C. Matthai, J. Phys.: Condens. Matter **10**, 1 (1998).
- ⁸Ph. Hofmann, K. C. Rose, V. Fernandez, A. M. Bradshaw, and W. Richter, Phys. Rev. Lett. **75**, 2039 (1995).
- ⁹G. D. Samolyuk and V. N. Antonov, J. Appl. Phys. **91**, 8540 (2001).
- ¹⁰B. N. Harmon and V. N. Antonov, J. Appl. Phys. **91**, 9815 (2001).
- ¹¹A. O. Pecharsky, K. A. Gschneidner, Jr., V. K. Pecharsky, and C. E. Schindler, J. Alloys Compd. **338**, 126 (2002).
- ¹²M. Born and E. Wolf, *Principles of Optics* (Pergamon Press, London, 1980), 6th ed.
- ¹³R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light* (North-Holland, Amsterdam, 1987).
- ¹⁴M. Schubert and W. Dollase, Opt. Lett. **27**, 2073 (2002).
- ¹⁵R. H. Graves, J. Opt. Soc. Am. **59**, 1225 (1969).
- ¹⁶D. E. Aspnes, J. Opt. Soc. Am. **70**, 1275 (1980).
- ¹⁷J. Szade and G. Skorek, J. Magn. Magn. Mater. **196**, 699 (1999).
- ¹⁸G. Skorek, J. Deniszczuk, and J. Szade, J. Phys.: Condens. Matter **14**, 7273 (2002).
- ¹⁹J. N. Hodgson and B. Cleyet, J. Phys. C **2**, 97 (1969).
- ²⁰J. L. Erskine and E. A. Stern, Phys. Rev. B **8**, 1239 (1973).