Studies on Growth, Optical, SEM and Laser Damage Threshold of L-Alanine single crystals for Non-linear Optical Applications

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Abstract

Organic nonlinear optical singe crystal of L-Alanine was grown by low temperature solution growth using water as solvent at room temperature. From the single crystal X-ray diffraction analysis, it crystallises in an orthorhombic system with space group $P2_12_12_1$. Various functional groups were identified by Fourier Transform Infrared Spectroscopic analysis (FT-IR). UV-Vis absorbance spectra shows that the lower cut off wavelength was observed at 240nm. Scanning Electron Microscope (SEM) studies reveals the surface morphology of the title material. The Laser Damage Threshold (LDT) for the grown crystal was tested using Nd : YAG laser. The Second Harmonic Generation (SHG) studies shows that the emission of green radiation confirms the NLO behaviour.

Key words: Single crystal growth – X ray diffraction (XRD) – Scanning Electron Microscope (SEM) – Laser Damage Threshold (LDT) – Second Harmonic Generation (SHG).

Introduction:

Nonlinear optical (NLO) materials capable of generating the second harmonic frequency, play an important role in the field of optoelectronics and photonics [1-2]. Organic materials are attractive due to their nonlinearities, ultrafast response, and high laser damage threshold [3-4]. Most natural amino acids individually exhibit then nonlinear optical properties [5] because they have a donor NH_2 and acceptor COOH and intermolecular charge transfer is possible.

L- Alanine (or) α- Alanine is an amino acid is used to make proteins and used in the biosynthesis process of proteins. It contains an amine group and a carboxylic acid group, both attached to the central carbon atom which also carries a methyl group side chain. The molecular structure of L-Alanine (CH_3-CH-NH_2-COOH) is shown in Figure 1.

In the Present study, L – Alanine single crystals were grown by slow evaporation solution growth technique using water as solvent. Further it was characterised by single crystal X – ray diffraction, FT- IR, UV – Vis absorbance. The Second Harmonic Generation (SHG) was tested by Kurtz-Perry powder technique. Further using SEM & EDAX the surface morphology and elemental composition were examined. Laser Damage Threshold was carried out and all the results were reported.

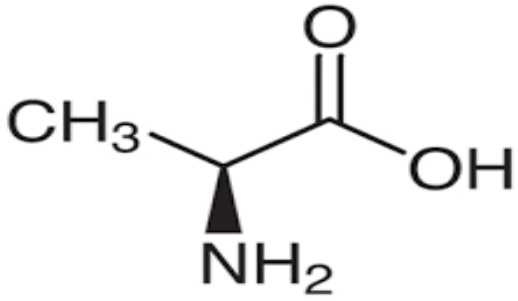

Figure 1. Molecular structure of LA

2. Materials and methods

2.1 Growth of single crystal

The commercial analytical available L - Alanine from (SRL pure 99%) was purchased and purified by repeated recrystallization process using water as solvent at room temperature. The solvent was taken in a beaker and the purified material was added gradually with continuous stirring for 5 hrs to get the saturation. The saturated solution was filtered using Whatman filter paper. The filtered solution was poured in a beaker and kept in an undisturbed position for slow evaporation. Transparent good quality single crystals of various sizes were harvested from mother solution after a time span of 30 days. The as grown single crystal is shown in Figure 2.

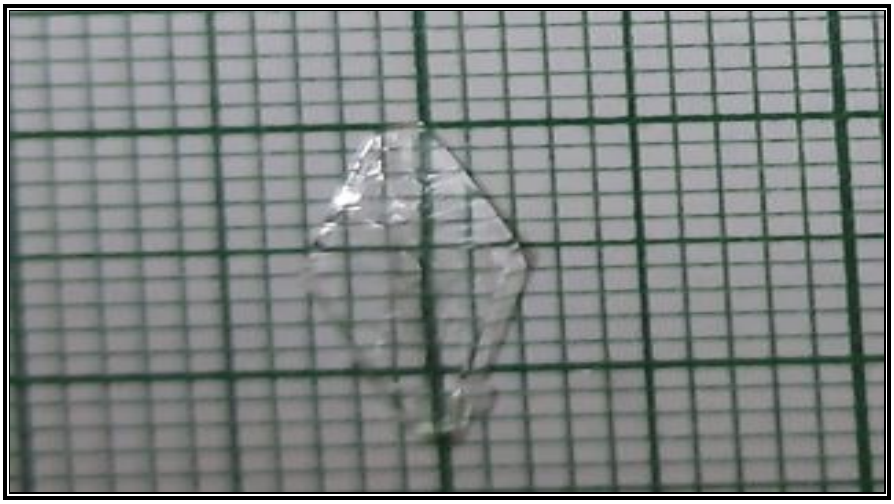

Figure 2. As grown single crystal of LA

3. Results and Discussion

3.1 Single Crystal X-ray diffraction Analysis

The as grown single crystal was subjected to Bruker Kappa X-ray diffractometer and the study reveals that the LA crystal belongs to Orthorhombic system with space group $P2_12_12_1$. The obtained lattice parameters are a = 6.032 Å, b = 12.343 Å, c = 5.784 Å; $\alpha = \beta = \gamma = 90°$ and volume 431 $Å^3$ is well matched with the reported literature [6] and tabulated in Table 1.

Table 1. Crystallographic information of L–Alanine

Chemical Formula	CH_3CHNH_2COOH
Molecular Weight	89.09 g/mol
Crystal system with Space group	Orthorhombic, $P2_12_12_1$
a	6.023 Å
b	12.343 Å
c	5.784 Å
$\alpha = \beta = \gamma$	90°
Volume	431 $Å^3$

3.2 FT-IR Spectral Analysis

FT-IR spectrum was recorded using BRUKER 66V FTIR spectrometer using KBr pellet technique in the range 400–4000 cm^{-1}. Figure 3 shows the recorded FT-IR spectrum of L - Alanine. Broad absorption bands observed at 3053 and 1584 cm^{-1} due to hydrogen bonded O–H stretching and C–H stretching of aromatic ring, respectively. The characteristic peaks at 2590, 2111, 1584, 1354, 856 and 539 cm^{-1} are due to asymmetric stretching, deformation and bending vibrations of N–H group.[7] In-plane deformation vibrations at 1111, 1015 and 856 cm^{-1} and out of plane deformation vibrations at 647cm^{-1} corresponds to the C–H group, confirming the ring structure is mono-substituted benzene. Among the major peaks the intense absorption at 1584 and 2590 cm^{-1} are attributed to C=O asymmetric stretching vibrations of COOH group. Aromatic ketones have absorption band due to the in-plane deformation vibration of the C–CO group at 539 cm^{-1}. Table 2 shows the FT-IR assignments of L – Alanine.

Table 2. Various Assignments of FT-IR spectrum.

Bond	Compound elements	Frequency Range
O=H	Monomeric – Alcohols, phenols	3640 – 3160
	Hydrogen bonded alcohols, phenols	3600 – 3200
	Carboxylic acids	3000 – 3300
N-H	Amines	3500 – 3300
		1650 – 1580
C – N	Amines	1340 – 1020
C=N	Nitriles	2260 – 2220
NO_2	Nitro compounds	1660 – 1500

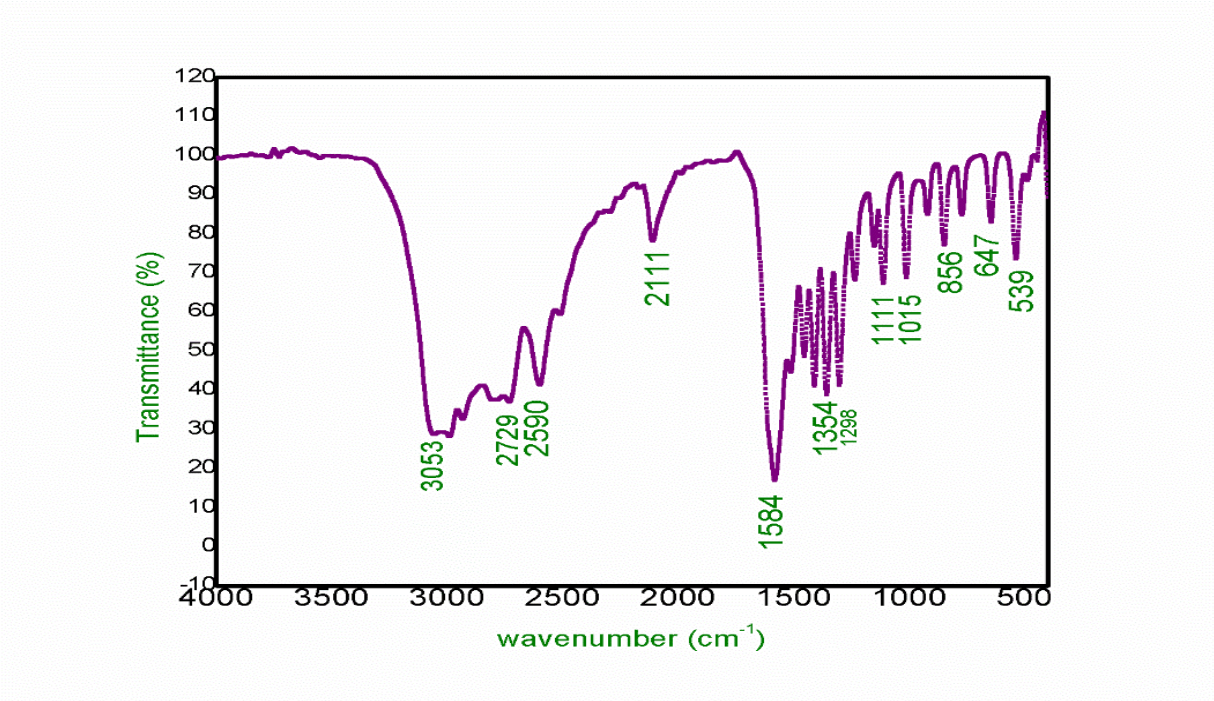

Figure 3. FT-IR Spectrum of LA

3.3 Optical Studies

3.3.1 UV- Vis absorbance analysis

Most of the molecules absorb ultraviolet or visible light. The absorbance of a solution increases as attenuation of the beam increases. UV – Vis absorption spectrum of the title material was recorded in the wavelength region 200-800 nm is shown in Figure 4. When absorbance is monitored from longer to shorter wavelength, the absorption is found to be nearly zero in the entire visible region of the spectrum. The lower UV cut-off of LA was found to be 240 nm. For a nonlinear optical material, transmission spectra are very important to the nature of the material and material should possess wide transparency range [8].

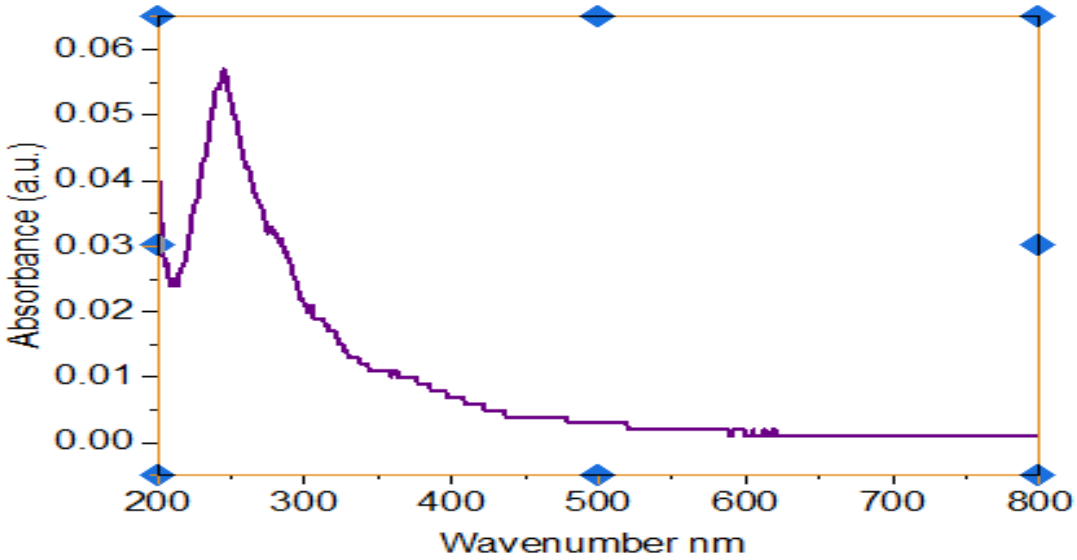

Figure 4. UV – Visible absorbance spectrum of LA

3.4 SEM and EDAX Studies

To examine the crystal topographical features and morphology, SEM studies were carried out with FEI-Quanta FEG 200F model. The resulted SEM image is as shown in Figure 5(a-d) it shows smooth surface having few inclusions with cluster like structure. The compositional inference about elements or chemicals in the crystal was look over through EDAX spectrometer which is resulted from electron back scattering from the sample [9]. Further, the EDAX spectrum (Figure 6) gives an information about the presence of the elements in the sample in qualitative manner.

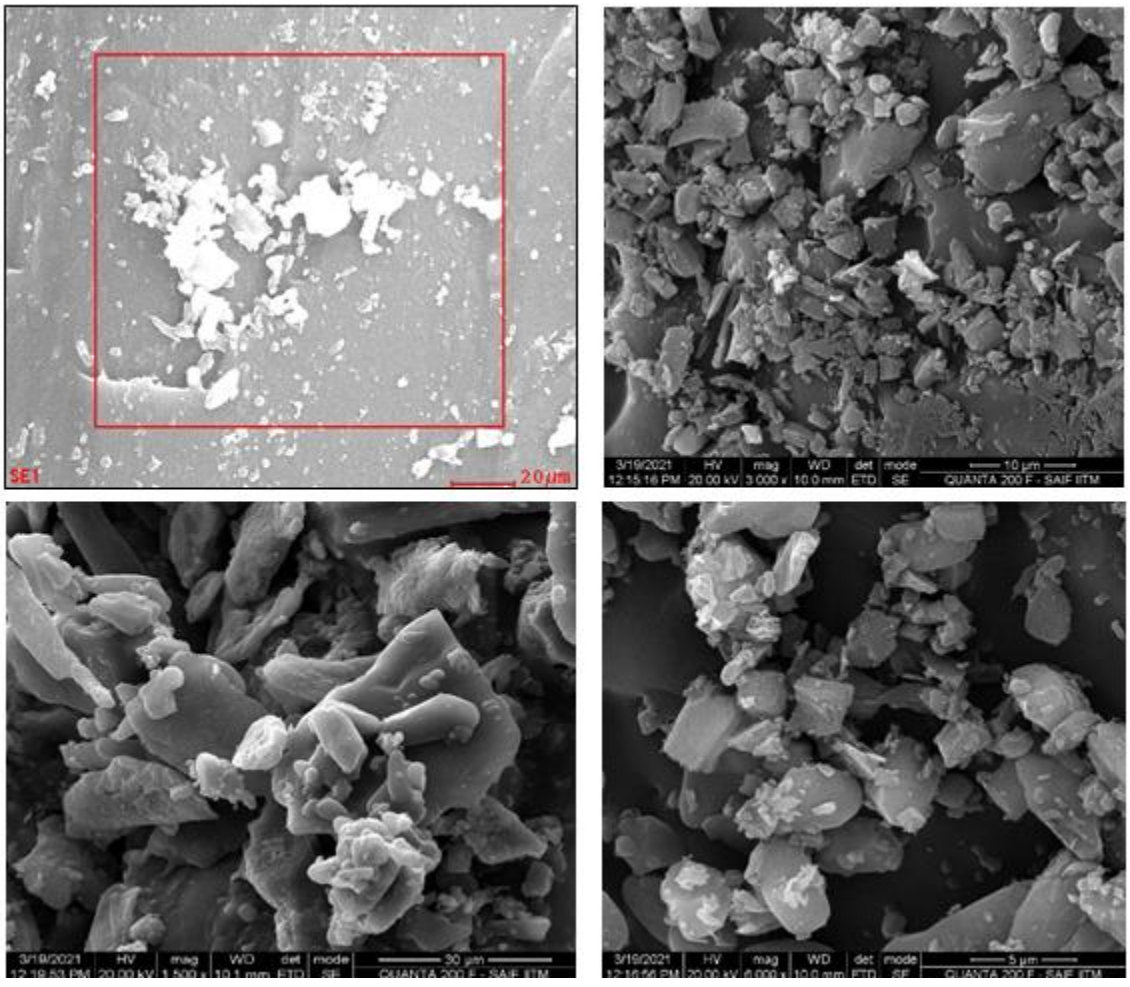

Figure 5a. SEM image of LA

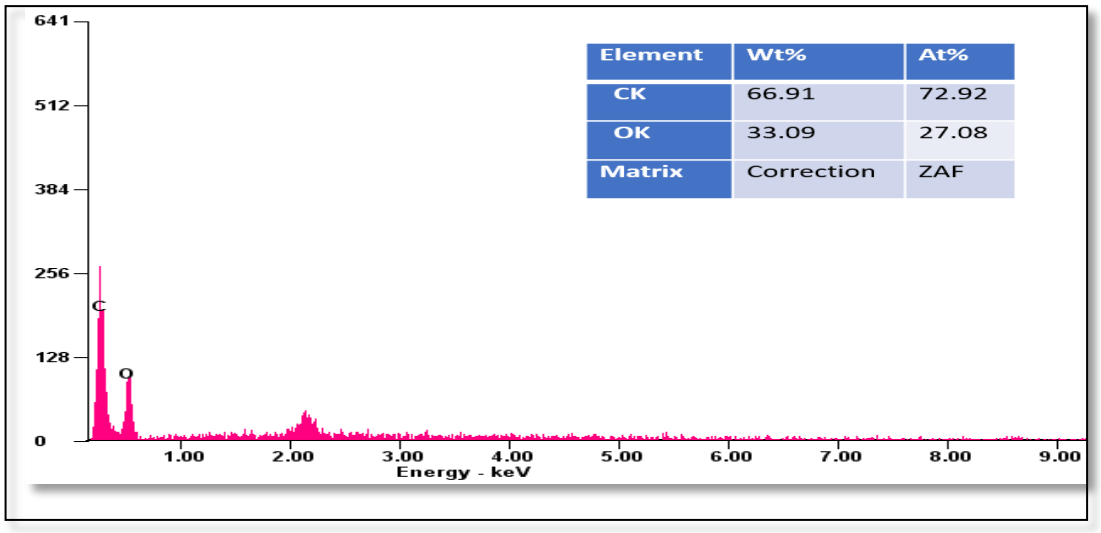

Figure 6. EDAX spectrum of LA

3.5 Laser Damage Threshold

For any nonlinear optical and laser applications, the laser damage threshold (LDT) value is an essential criterion for practical devices, because it gives the limit of performance in the optical system. For any applications, the materials must have ability to withstand for the given laser energy. But the materials may have laser induced bulk damage due to many reasons of intrinsic and extrinsic factors. Intrinsic damage limits the optical strength of materials that includes linear absorption, some nonlinear effects such as self-focusing, multi-photon absorption or two photons absorption, stimulated Brillouin scattering, stimulated Raman scattering, and electron avalanche break down. On the other hand, extrinsic damage includes material defects/voids, impurities and finished surface of materials. Also it affects the internal laser parameters such as pulse width, beam spot size, transverse and longitudinal laser modes and laser wavelength. Hence, the high optical surface damage tolerance is extremely important in the performance of nonlinear optical (NLO) and optoelectronic device applications [10]. In the present study, the laser damage threshold value of LA crystal was measured using a Q-switched Nd: YAG (1064 nm) laser operating in transverse mode (TM00) and pulse width of 6 ns in the frequency rate of 10 Hz. Laser beam diameter of 1mm was used to irradiate on the well-polished LA crystal surface. The output laser beam was controlled with a variable attenuator and that crystal was placed at the focus of the converging lens of focal length 10 cm. During the laser irradiation, damage of the surface can be determined by the visual formation of damage and the input laser energy density was recorded by a power meter. The surface damage threshold of the grown LA crystal was calculated using the following expression [11-12]. Power density $Pd = Ep / \tau \pi r^2$. The calculated laser damage threshold value of title material is 4.13 GW/cm^2, which is compared to the some of the standard NLO materials. It can be concluded that the grown crystal has good optical damage tolerance and compared with other crystals are tabulated in Table 3. Thus, the LA crystal is useful for high power laser applications.

Table 3. LDT values of L-Alanine with reported NLO crystals

Crystal Name	Laser damage threshold	Reference
L-Alanine (LA)	4.13 GW/cm^2	Present study
KDP	1.8 GW/cm^2	[13]
L – Histidine Bromide	1.32 GW/cm^2	[14]

3.6 Second Harmonic Generation Studies

Being one of the principal methods of measuring NLO features, Kurtz Perry powder techniques [15] involves the microcrystalline substance on which the laser beam is made to fall resulting in the generation of second harmonic wave. Thus, received beam is filtered and detected and compared with KDP reference. Accordingly, in the present work, Q-switched Nd:YAG Laser having power of 1.5 mJ/pulse to 3J was used. Title material was well grounded to the identical particle size being 125– 250 µm and then taken in the microcapillary tube. The powder of KDP of same particle size was used for reference. The SHG was proved by the green light emission (wavelength 532 nm), and the efficiency of second harmonic generation is found to be 0.4 times greater than that standard KDP

4 Conclusions:

Good quality organic NLO crystal of L- Alanine single crystals were successfully grown using the solvent evaporation technique at room temperature. The grown crystal has been subjected to structural and optical characterization. The X-ray diffraction analysis confirmed the orthorhombic structure with space group $P2_12_12_1$. Various functional groups have been identified by the FTIR spectral analysis. From the UV-Vis absorbance data, the lower cut off was observed at 240nm in the UV region exhibit the good optical quality of the material, shows its suitability for the fabrication of various optoelectronic devices.

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References

[1] R.W. Boyd, Nonlinear Optics, Academic Press, San Diego, **1992.**

[2] B.E. Saleh and M.C. Teich, Fundamentals of Photonics, Wiley, New York, **1991.**

[3] R.L.Sutherland, Hand Book of Nonlinear Optics, Dekker, NewYork, **1996.**

[4] D.S.Chemla and J.Zyss(Eds.), Nonlinear Optical Properties of Organic Molecules and Crystals, Academic Press, NewYork, **1997** 1& 2**.**

[5] M.Parthasarathy, M.Anantharaja and R Gopalakrishanan, Growth and characterization of large single crystals of L-serine methyl ester hydrochloride"Journal of Crystal Growth, **2012,** 340, 118-122,**.**

[6] Harry J. Simpson and Richard E. Marsh, Crystal structure of L-Alanine 20 (1966) 550. Acta Cryst. **1966,** 20, 550-555.

[7] P. Anitha and N. Muruganantham Growth and Characterization of L-Alanine Crystals using FT-IR, UV Visible Spectra International Journal of Science and Research, **2014,** 3(3), 51-56.

[8] M. Parthasarathy and R. Gopalakrishnan, Growth and characterization of Methyl 2-amino-5-bromobenzoate crystal for NLO applications, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, **2012**, 97, 1152–1158.

[9] M. R. Hareeshkumar, G. J. Shankaramurthy, A. Alhadhrami, M. R. Jagadeesh and B. M. Prasanna, Growth, Characterization and NLO Property Study of Doped L-Alanine Crystal, Iranian Journal of Science and Technology, Transactions A: Science, **2021**, 45, 1843–1850

[10] G.H. Sun, G.H. Zhang, Z.H. Sun, X.Q. Wang and D. Xu, Mater. Chem. Phys. **2011**, 127, 265–270.

[11] N Mahalakshmi and M Parthasarathy, Spectral, Laser Damage Threshold, Second Harmonic Generation and Antibacterial activities of Hippuric acid single crystals NeuroQuantology, **2022**, 20(15), 6779-6785.

[12] P. Malliga, C. Alosious Gonsago and A. Joseph Arul Pragasam, "Growth and characterization of Glycyl L – Alanine single crystals for NLO devices", Material Science An Indian Journal, **2013,** 9(11), 428 – 432,.

[13] N.Vijayan, G.Bhagavannarayna, R.RameshBabu, R.Gopalakrishnan,, K.K.Maurya and P.Ramasamy, Cryst.Growth Des, **2006**, 6, 1542-1546.

[14] M. Krishna Mohan, S. Ponnusamy and C. Muthamizhchelvan, Spectral, optical, etching, second harmonic generation (SHG) and laser damage threshold studies of nonlinear optical crystals of l-Histidine bromide, Applied surface science, **2018**, 449, 92-95.

[15] S.K. Kurtz and T.T. Perry, A powder technique for the evaluation of nonlinear optical materials, Journal of Applied Physics, 39, **1968,** 3798–3813.