Electric Studies on Polyvinyl Alcohol with Additions of Magnesium Sulfate

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ABSTRACT: Polyvinyl alcohol (PVA; molecular weight 17,000 g/mol) with additions of several different amounts of magnesium sulfate (molecular weight 246.945 g/mol) was prepared by the casting technique. The dc electric properties of these films were measured in different temperature ranges and the activation energy values as a function of different magnesium sulfate amounts were calculated. The dependency of dc electrical conductivity σ_{dc} at a certain temperature was found to fit the well-known equation $\sigma_{dc} = [(1/R) \times (t/A)]$ $(\Omega^{-1}\ m^{-1})$. The temperature dependency of σ_{dc}, which suggested an electronic hopping conduction mechanism in a thermally assisted electric field, in addition to some theoretical mechanism were discussed. Also the values of activation energy as a function of different amounts of magnesium sulfate were investigated and it was found that the activation energy values for most samples increase with increased amounts of magnesium sulfate. On the other hand, the nonlinear coefficient parameter as a function of the different amounts of magnesium sulfate was investigated for all the prepared samples. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3167–3173, 2004

Key words: polyvinyl alcohol (PVA); conducting polymers; magnesium sulfate; activation energy; nonlinear polymers

INTRODUCTION

Magnesium is the eighth most abundant natural element.[1] It makes up 2.5% of the earth's crust and is commonly found in such minerals as magnesite, dolomite, olivine, serpentine, talc, and asbestos. Also greater attention has been focused on polyvinyl alcohol (PVA) because it is considered a leader in the industry since its discovery in the year 1924 because of its unique chemical and physical properties as well as its industrial applications.[2–9] Moreover, PVA is an interesting material and several research workers have shown considerable interest on it (Varma et al., 1983; Henisch, 1983; Rashkovich, 1991; Udupa et al., 1997; Freeda and Mahadevan, 2000[10]). The necessity for stable and reliable PVA has greatly increased during recent years.[2–5] In this connection the study of PVA with additions of different amounts of magnesium sulfate, compounds of which are involved in many uses, is very important, particularly with respect to a knowledge of any changes in its electrical properties. A research program on the growth and electrical properties of pure PVA and PVA to which impurities have been added is being carried out in our laboratory. As part of the program we have investigated all the electrical, dielectric, optical, mechanical, and thermal effects of magnesium sulfate when it is added to pure PVA.

The electrical characteristics of polyvinyl alcohol and magnesium sulfate are considered attractive properties that provide a basis for further in-depth study. One of the main studies of the electric properties of polymeric materials is to obtain information on molecular motion and structural transitions. The optical and mechanical properties of PVA with different amounts of magnesium sulfate were previously studied,[11–13] although to my knowledge there have been no published systematic studies of the influence of magnesium sulfate on the electrical properties of PVA.

The purpose of this article is to offer an extensive and more thorough study of the dc electrical conductivity (σ_{dc}) and some other parameters for commercial PVA of molecular weight 17,000 g/mol with different amounts of magnesium sulfate under temperature range (293–393 K). Results obtained in the present study are discussed in detail.

EXPERIMENTAL

Sample preparations

Polyvinyl alcohol (PVA; molecular weight 17,000 g/mol; BDH, Poole, UK) was used as a basic polymeric material along with different amounts of magnesium sulfate ($MgSO_4 \cdot 7H_2O$; molecular weight 246.945 g/mol; designated as MS in this study). Solutions of PVA and MS were prepared by dissolving

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TABLE I
Polyvinyl Alcohol and Magnesium Sulfate Ratios

Symbol	Polyvinyl alcohol ratio (%)	Magnesium sulfate ratio (%)
MP0	100	0
MP1	95	5
MP2	90	10
MP3	85	15
MP4	80	20

both in bidistilled water and maintained for 24 h at room temperature to swell. The solution was then heated to 333 K using a drying furnace and thoroughly stirred using a magnetic stirrer for 20 h until the polymer solution became completely soluble. The solution was poured into flat glass plate dishes (diameter 7.5 cm) at room temperatures. Homogeneous films from PVA/MS were obtained after drying in the same furnace for 48 h at 313 K. All the products of this

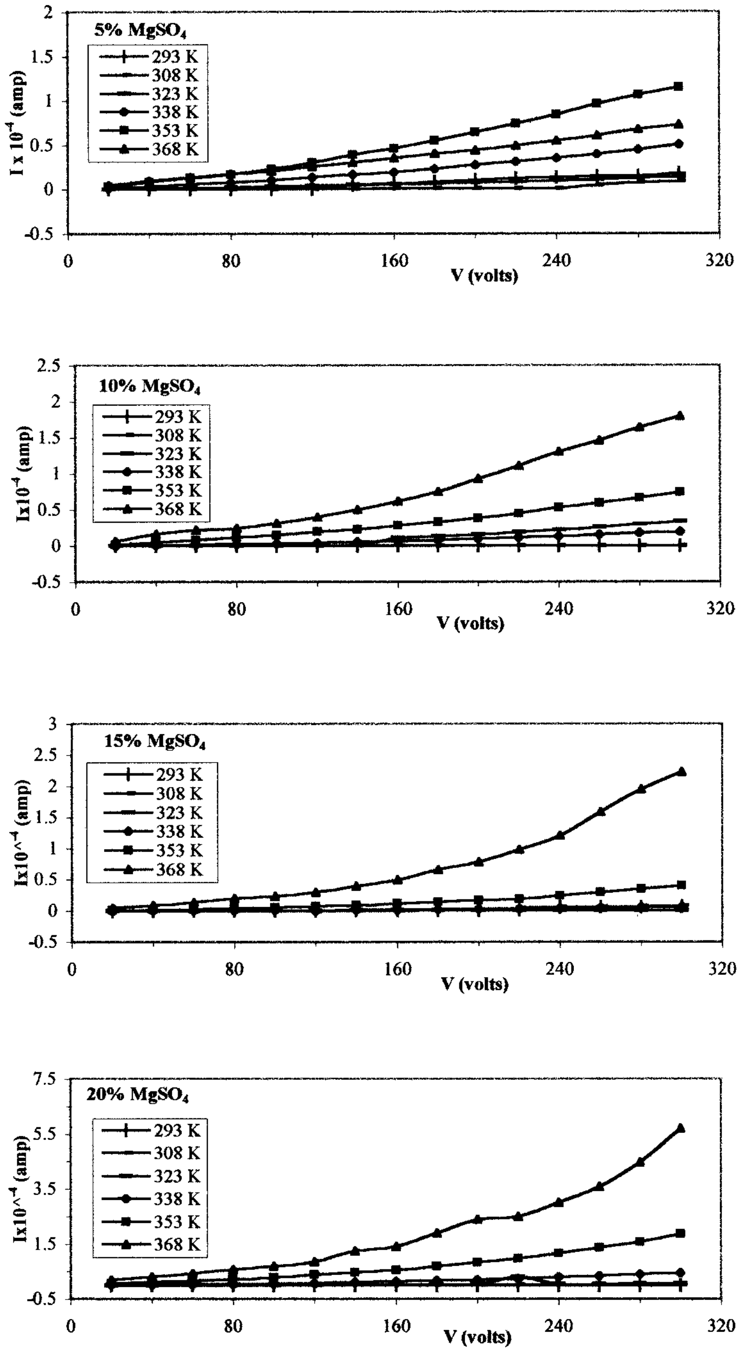

Figure 1 Current–voltage characteristics for different additive samples of (PVA + $MgSO_4$).

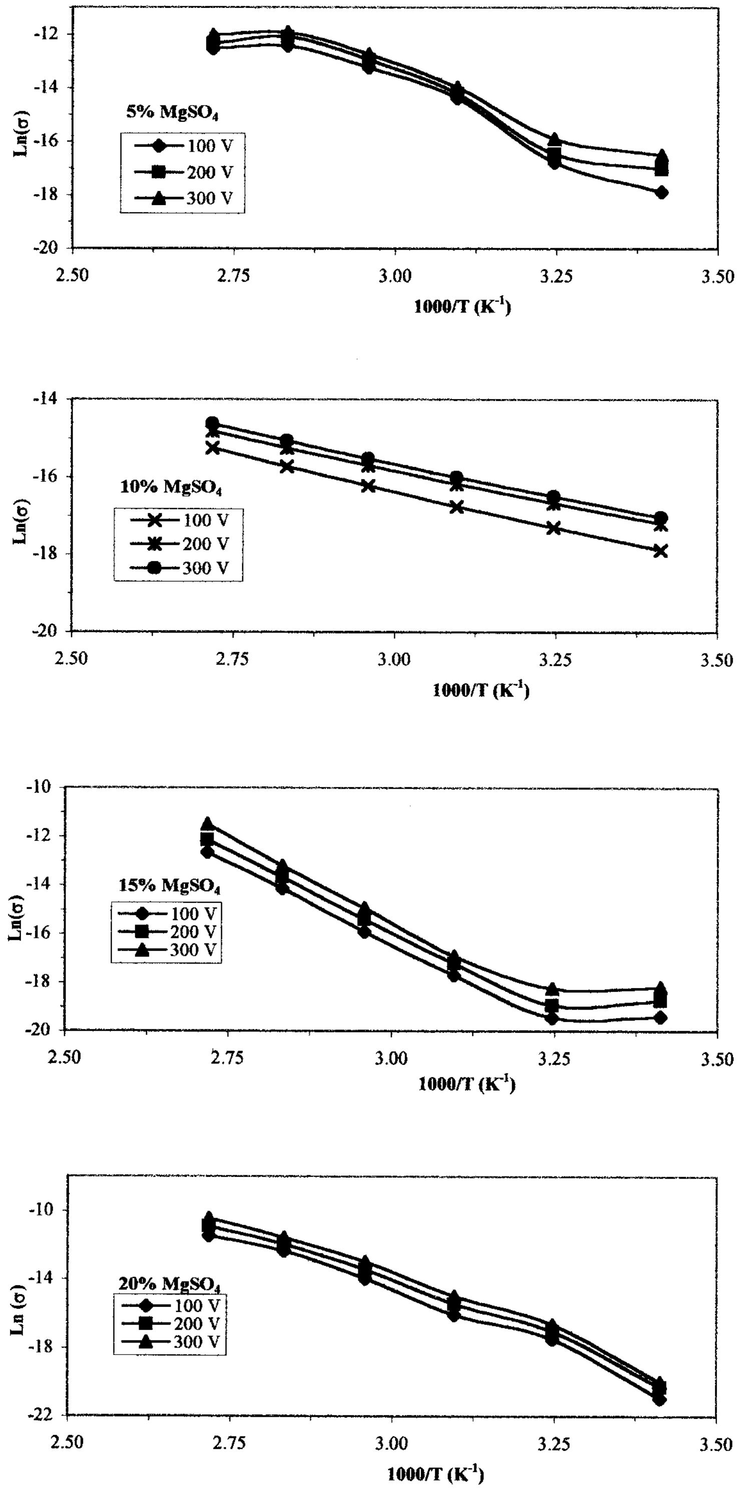

Figure 2 Plots of ln(DC conductivity) versus reciprocal absolute temperature for different samples of (PVA + $MgSO_4$) at different voltages.

mixture were found to be very stable, colorless, odorless, and transparent. Only the products with very high transparency were selected and used for the electrical conductivity and all other measurements. The thickness of the produced films was around 0.21 mm. The selected films were divided into five groups, denoted by MP0, MP1, MP2, MP3, and MP4 corresponding to 0, 5, 10, 15, and 20% magnesium sulfate ratio in the mixture, respectively (Table I), where MP0 means pure polyvinyl alcohol.

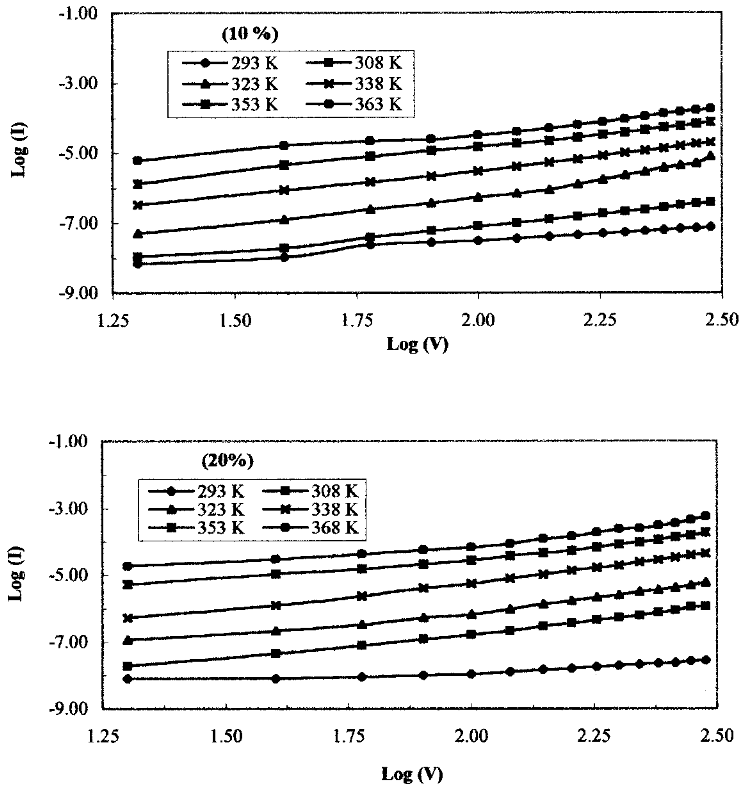

Figure 3 Plots of nonlinear coefficients for samples of PVA with different amounts of magnesium sulfate as additives at different temperatures.

Electrical measurements

PVA/MS samples were cut from the mother films into disk shapes (diameter 1 cm). The disks were well coated on both sides with silver paint to ensure good electrical contact between the two electrodes of the sample holder. The cell used for the electrical measurements consisted of four stainless-steel rods (10 cm long). Also two stainless-steel disks served as top and bottom bases for the four rods and many small ceramic parts were included for insulating purposes. The samples with the cell were put inside an electrical furnace contact with a digital thermometer just in contact with the sample to measure the temperature of the sample only, without any temperature gradient. The accuracy of measuring temperature of the sample was better than 0.2 K. The temperatures used varied over a range of 273–500 K with a temperature control of ±0.5 K. Very fine copper wires were cemented on both surfaces of the holder with the paint and the specimen was mounted on a sample holder. The direct current values I in amperes, the applied voltage between the two ends of the samples V in volts, and thus the resistance R in ohms for all samples were automatically measured using a Keithley 616 digital electrometer (Keithley Metrabyte, Taunton, MA), as shown in Figure 1. This figure shows the I–V measurements for all samples were performed under atmospheric conditions. Under these conditions the resistance values of the different samples were estimated, as was the dc electrical conductivity as a function of temperature $\sigma_{dc}(T)$ for all samples at three different voltages (100, 200, and 300 V), as shown in Figure 2.

Also, we studied the relationships between magnesium sulfate ratios of the samples and the dc electrical conductivity at different temperatures, as shown in Figure 3. From this figure, we see that the effect of the different amounts of magnesium sulfate on PVA samples on the conductivity fluctuates and generally the conductivity was shifted to lower temperatures.

RESULTS AND DISCUSSION

Current–voltage characteristics

A decreasing tendency may be observed in resistance values for the samples with high additions of magnesium sulfate. This suggests that the dramatic change of resistance depends on the magnesium sulfate ratio in the samples.

After studying the relationship between the dc values and the applied voltage for all samples, as shown in Figure 1, we next determined the dc conductivity σ_{dc} values from the parameters of thickness (t in m) of

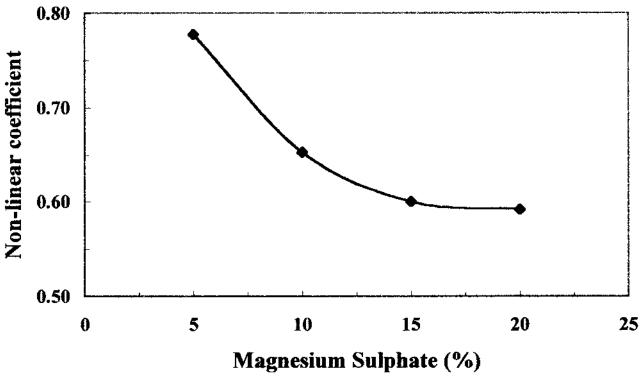

Figure 4 Plot of nonlinear coefficient parameter against magnesium sulfate ratio in PVA/$MgSO_4$ samples at 338 K.

the sample, its cross-sectional area (A in m^2), and its resistance (R in Ω) separately using the following very familiar equation:

$$\sigma_{dc} = \left(\frac{1}{R} \times \frac{t}{A}\right) (\Omega^{-1}\ m^{-1}) \qquad (1)$$

Therefore the relationships of dc electrical conductivity with temperature $\sigma_{dc}(T)$ for all PVA/MS sample mixtures were carefully measured using a Keithley electrometer, as mentioned earlier. However, the dc electrical conductivity σ_{dc} is simply $\sigma_{ac}(\omega)$ in the limit $\omega \rightarrow 0$.

The dc electrical conductivity as a function of temperature $\sigma_{dc}(T)$ for all the samples at three different voltages was investigated and the results are shown in Figure 2, from which the relationship of dc electrical conductivity values with the reciprocal of temperature, observed for all samples investigated, shows a slightly decreasing rate. In the lower temperature range, the conduction mechanism can be attributed to electron hopping under the effect of the electric field. By increasing the temperature above 323 K, the thermal activation is more effective and polarization conduction, in addition to electrons hopping over a barrier in the thermally assisted electric field, can be expected. For all samples shown in this figure, we note that values of $\sigma_{dc}(T)$ exhibit a constantly increasing rate over the entire temperature range studied.

A logarithmic format for both current and voltage is known to be clearer than a linear representation, which tends to exaggerate the nonlinearity in proportion to the current scale chosen, as shown in Figure 3. From the following empirical formula[14,15] we deduced the values of the nonlinear coefficient for different samples:

$$I = KV^{\alpha} \qquad (2)$$

TABLE II
Activation Energy Values for Different Additives of ($PVA + MgSO_4$) Samples at Different Voltages

Voltage (V)	Activation energy (eV)				
	MP0	MP1	MP2	MP3	MP4
100	0.33	0.40	0.74	0.90	1.16
200	0.30	0.41	0.68	0.89	1.15
300	0.30	0.45	0.64	0.88	1.16

where K is a constant and α is the nonlinear coefficient parameter.

Also, we plotted the nonlinear coefficient parameter against magnesium sulfate ratio in the samples at different temperatures (Fig. 4). It may also be observed from this figure that the value of α decreases with increasing magnesium sulfate contents in the samples.

Activation energy

The activation energy values for all samples were also calculated from dc electrical conductivity and absolute temperature curves. The values of activation energies were derived by calculating the slopes in the plots in Figure 2, which follow the well-known Arrhenius law:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) (S\ m^{-1}) \qquad (3)$$

where σ_0 is a preexponential factor depending on the material, E_a is the activation energy for conduction, T is the absolute temperature, and k_B is the Boltzmann's constant. The activation energies of all samples were estimated using the slopes of the above plots (E_a

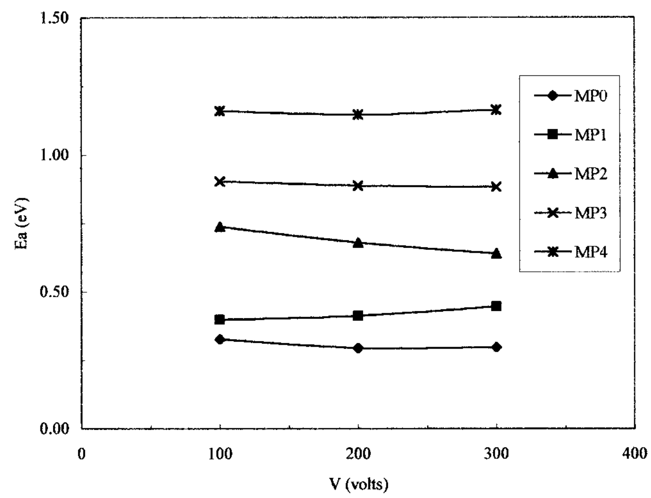

Figure 5 Plots of activation energy versus applied voltages for different samples of magnesium sulfate additives to PVA.

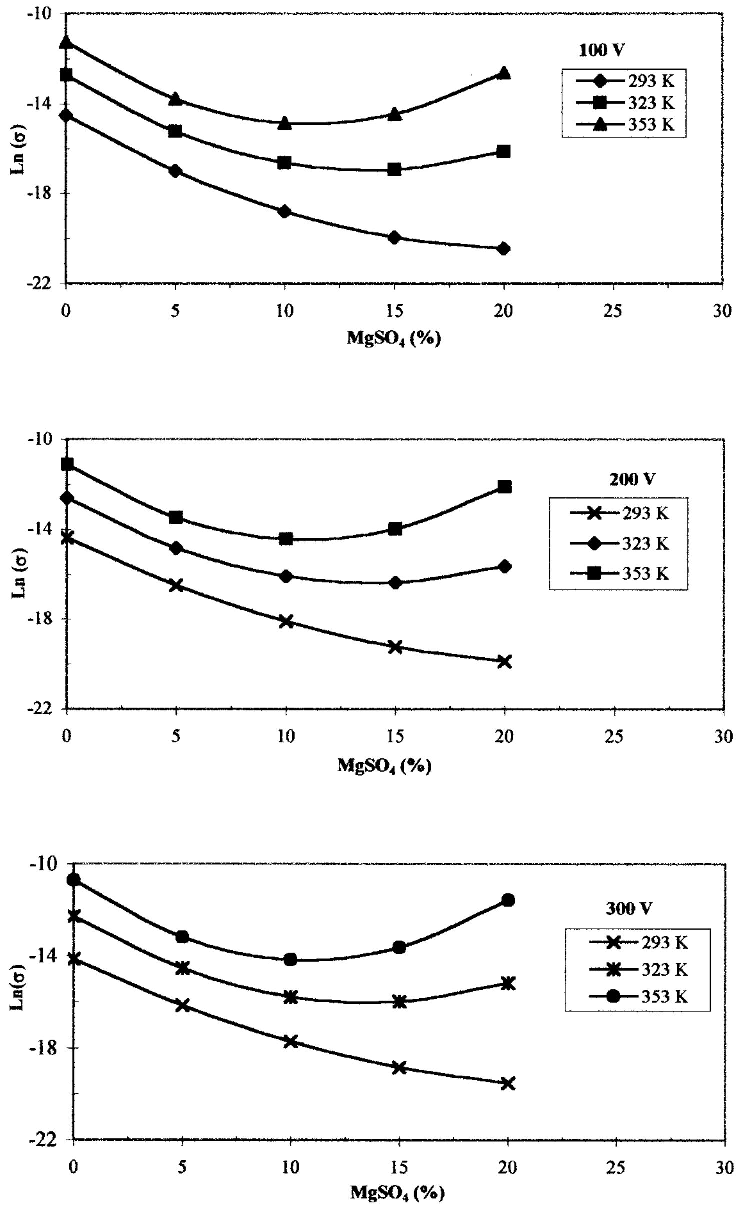

Figure 6 Relationships between $MgSO_4$ ratios in MP samples and ln(conductivity) at different voltages.

$= -\text{slope} \times k_B$). The calculated data for activation energies are summarized in Table II. The activation energy for all samples against applied voltages are shown in Figure 5. The steady-state values so obtained become more meaningful if presented as Arrhenius plots according to the above law, from which the activation energy E_a was obtained. Although the absolute values of E_a vary from sample to sample and depend on magnesium sulfate ratio, the general increase with increasing ratio is the same in all samples.

Effect of magnesium sulfate ratios

From studies of the relationships between magnesium sulfate ratios in different samples and the dc electrical conductivity, as shown in Figure 6, we found that the variation in the different contents of magnesium sulfate in these samples has a slight, but important, influence on the electrical conductivity in this range studied.

CONCLUSIONS

Mixtures of pure polyvinyl alcohol (PVA) and varying amounts of magnesium sulfate ($MgSO_4{\cdot}7H_2O$) were prepared and both electrical conductivity and activation energy were measured at various temperatures ranging from 293 to 368 K. The dc electrical conductivity of PVA with additives of $MgSO_4$ occurs between the normal conductivities of semiconductors and insulators. The electrical conductivity followed the Arrhenius law with activation energies between 0.33 and.1.16 eV for the different samples. Experimental evidence for the correlation between the conductivity and the activation energy in the bulk state was obtained. Also the nonlinear coefficient parameter was studied and thoroughly investigated.

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