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Effect of Salts and Dissolved Gas on Optical Cavitation near Hydrophobic and Hydrophilic Surfaces

N. F. Bunkin,[†] O. A. Kiseleva,[‡] A. V. Lobeyev,[†] T. G. Movchan,[‡]
B. W. Ninham,[§] and O. I. Vinogradova^{*,‡}

Department of Wave Phenomena, Institute of General Physics, Russian Academy of Sciences, 38 Vavilova Street, 117 942 Moscow, Russia, Laboratory of Physical Chemistry of Modified Surfaces, Institute of Physical Chemistry, Russian Academy of Sciences, 31 Leninsky Prospect, 117 915 Moscow, Russia, and Department of Applied Mathematics, Australian National University, Canberra 0200, Australia

Received March 19, 1996. In Final Form: January 22, 1997[®]

The effect of four 1:1 electrolytes (KCl, KBr, NH₄Cl, and CH₃COONa) on optical (stimulated by laser pulse) cavitation in thin layers bounded by hydrophobic and hydrophilic surfaces has been explored. For water and all salts (up to 1 M) in the case of hydrophobic surfaces, the cavitation probability is enhanced as compared with the case of hydrophilic walls. The increased cavitation probability observed with hydrophobic surfaces can be linked to an enhanced concentration of gas-filled submicrocavities close to them. The phenomenon seems to depend strongly on dissolved gas. Variations in the probability of cavitation that occur with electrolyte are significant and depend on its concentration and type. The specific effect of electrolytes on optical cavitation in a thin layer likely makes sense only in terms of the previously neglected ionic dispersion interactions. The results obtained may have implications for the mechanisms of the long-range hydrophobic interactions between surfaces and hydrophobic slippage.

I. Introduction

Hydrophobization of a solid surface plays a role in phenomena like adhesion, wetting, film stability, cavitation, and coagulation. Hence the solid hydrophobic surface and the nature of liquids adjoining it are the subject of much interest. Especially in the last decade with the advent of new techniques, it has been intensively studied.

Most experimental investigations have focused on direct measurements of the force–distance profiles between macroscopic hydrophobic bodies. These measurements have revealed the presence of strong attraction (orders of magnitude larger than the van der Waals force) and extremely long range (measurable to 100 nm).^{1–5} The existence of an interaction at such distances challenges fundamental notions on liquid structure, and despite considerable theoretical efforts, the origins of these long-range attractions remain controversial. There have been several theoretical attempts to explain the phenomena. The first approach is based on water structural effects.^{6,7} However, these theories are unlikely to be able to explain the long-range nature of interaction. Other ideas invoke electrostatic interactions to account for the range, and various origins for the strength of the attraction.^{8–10} These

electrostatic theories predict the interaction should scale with a range of twice the inverse Debye length of the electrolyte. Sometimes, this salt dependence is observed, e.g. ref 11. However it is not valid in general.¹² A more recent proposal, focusing on the observed cavitation of the water when the hydrophobic surfaces are separated from contact,¹³ involves the metastability of the film due to its confinement between hydrophobic walls,¹⁴ or separation-induced phase transition.¹⁵ It has also been recently argued that the presence of dissolved gas in the aqueous medium has been implicated as the source of the long ranged hydrophobic attractions.^{16–18}

Again, in parallel and equally mysterious is the phenomenon of slippage of water over a hydrophobic surface.^{19,20} This also depends on the dissolved gas being in a different form^{18,21,22} and on the change in viscosity of the solvent near the hydrophobic wall.²³

Various indirect observations, differences in the stability of emulsions, hydrophobic suspensions, filtration of fine hydrophobic particles, latex polymerization gassed or degassed, and ion binding to micelles also implicate a role for dissolved gas.^{24–26}

* To whom correspondence should be addressed.

[†] Institute of General Physics, Russian Academy of Sciences.

[‡] Institute of Physical Chemistry, Russian Academy of Sciences.

[§] Australian National University.

® Abstract published in *Advance ACS Abstracts*, April 15, 1997.

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Recently we have obtained some results that may add a new dimension to the problem. Laser-induced optical cavitation^{27,28} suggested that there exist in aqueous bulk electrolyte solutions (and indeed in other liquid systems²⁹) long-life charged submicrocavities—bubstons.³⁰ Their size appears to be of the order of nanometers.³² Consequently (although we do not, and cannot, claim universality), the measured probability of optical cavitation (breakdown)³³ can serve as an indirect method of investigation of the relative change in concentration of gas-filled submicrocavities (see ref 27). In previous work¹⁸ we explored optical cavitation in a thin water layer confined between two hydrophilic, and especially two hydrophobic, walls. In the case of hydrophobic surfaces, we observed the increased cavitation probability that can be linked to an enhanced concentration of gas-filled submicrocavities. The aim of the present paper is to explore the effect of electrolytes and dissolved gas on optical cavitation near hydrophobic and hydrophilic surfaces. Here we limited ourselves to aqueous solutions of several 1:1 electrolytes. The choice of the salts and of the range of their concentrations was partly motivated by some curious observation of salt dependence of coalescence of macrobubbles:¹⁶ It was found that some electrolytes reduce the macrobubble coalescence at high concentration (above ~ 0.2 M), whereas others have no effect. These results could indicate that the ions may be important in their effect on water structure rather than for any further electrostatic effect (which is consistent with the bubston model) and that this ion-induced water structure could be connected with hydrophobic attraction (in the case of ref 16 it occurs between macrobubbles). For some electrolytes the coalescence phenomenon correlates with the surface tension changes,³⁴ but it is also likely that submicrobubble gradient between macroscopic bubbles could play an important role in the coalescence process.³⁵ Thus, here we try to explore optical cavitation of just the salt pairs that affect macrobubble interactions differently. The differences observed with solutions between hydrophobic and hydrophilic surfaces seem to be quite dramatic and suggest a

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(30) In this approach the problem of the diffusion stability of submicrobubbles arises. In conventional theories, the latter must always dissolve because the pressure inside the submicrobubble is higher than that in surrounding solution.³¹ Generally speaking, the question of the diffusion stability of a submicrobubble remains unresolved. However, the charge of a submicrobubble can, in principle, provide a possibility for its diffusion stabilization. Namely, the existence of submicrobubbles could depend on a balance of Laplace pressure; with an unknown surface tension γ (that we know must be less than the planar value, 72 dyn/cm, and greater than the limiting value $\gamma = 0$ at zero radius) against an opposing electrostatic pressure.³² This is why such submicrobubbles together with their ionic shells were termed bubstons (i.e. bubbles stabilized by ions). The possibility of ion and ion pair adsorption on the liquid/gas interface will be commented on when discussing our results.

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(33) The optical cavitation is the formation of a macroscopic bubble, while the breakdown is the formation of laser plasma under a laser pulse. The optical cavitation should be considered as the first stage of the optical breakdown, because the spark itself is formed only inside this macroscopic bubble.²⁷ For plasma formation the proper fluency of laser radiation is required, so that optical breakdown may be observed only inside the focal volume of the lens, provided that focusing is rather tight.

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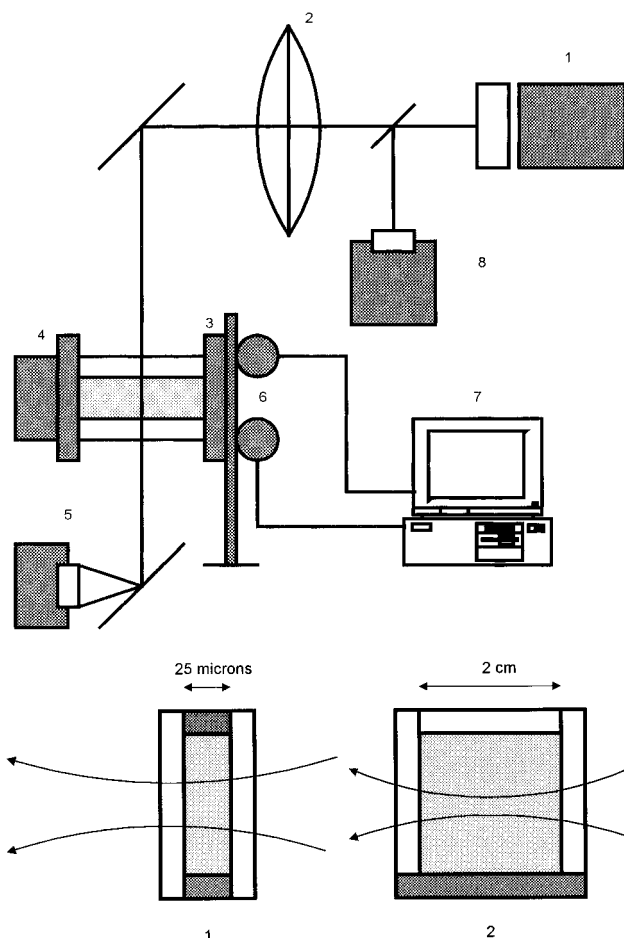


Figure 1. (top) Schematic diagram of the setup for investigation of optical cavitation: (1) YAG:Nd³⁺ laser; (2) lens; (3) cuvette; (4) thermostat; (5) microscope; (6) two-coordinate table; (7) computer; (8) radiation energy measuring device. (bottom) Cuvettes for the cavitation study: (1) thin cuvette (first design); (2) thick cuvette (second design).

possible connection between dissolved gas, electrolyte, hydrophobic interaction, and slippage over a hydrophobic wall.

II. Materials and Methods

A. Optical Cavitation Measurements. Optical cavitation was investigated with an experimental setup which has been used in a few previous studies^{18,29} (see Figure 1). A radiation pulse in the single transverse mode of a pulse-repetitive YAG: Nd³⁺ laser (wavelength $\lambda = 1.06 \mu\text{m}$ and pulse duration $\tau = 11.5$ ns) with a fixed amount of energy was isolated from the train of pulses and directed by a lens into a cuvette. Two designs of cuvette were used.

The first design was the same as in previous studies;^{18,29} i.e., the cuvette consisted of two polished glass plates separated by a Teflon lining 25 μm thick with a confined drop of water or water–electrolyte solution. The plates were fastened to each other by the aid of metallic fixtures provided with water jackets connected to a liquid thermostat. The temperature of the thermostat was maintained at 20° with a precision of ± 0.1 °C. It is clear that, for studying the cavitation in a thin cuvette, the focal volume of the lens used should be located outside of it. In our experiments the cuvette was mounted before the focus. As a result, the diameter of the laser spot inside the cuvette was approximately 1 mm; i.e., the focusing was not tight. This led to a laser beam intensity that was sufficient to induce formation of cavitation (macro)bubbles. At the same time such a focusing prohibited the formation of a laser spark (on cavitation there was no breakdown proper) at the water–electrolyte solution/glass interface, so that there was no strong thermal action. The cuvette area shot by laser pulses was located within the objective

field of an optical microscope, through which the presence of cavitation from a laser pulse was determined. We also checked with the microscope that the windows were not damaged in the process, and the solutions were not spoiled. The cuvette itself was mounted on a program-controlled, movable two-coordinate table, serving to move the cuvette into the plane perpendicular to the laser beam. After emission of each laser pulse the cuvette was shifted to a new site, and a new shot was made.

The second design of the cuvette was designed for the investigation of the relative change in the optical breakdown probability close to the liquid/air interface as compared to the bulk case. In this case the cuvette was of a larger size, and the focal volume was situated inside the cuvette. We remark here that, in spite of the fact that the focusing was rather tight, there was no influence of the laser beam on the cuvette walls. The focal volume here was located at a distance about 1 cm from the cuvette walls, while the front of high pressure and temperature diminishes steeply at a distance of several millimeters from the center of the laser plasma flash. In this case, the program-controlled movable table also served to shift the cuvette in the vertical direction, so that we were able to study the breakdown probability at different levels of the cuvette, including the region near to the interface with air. We remark here that, due to the concave form of the meniscus in the cuvette, we were able to direct the laser beam at a tangent to the liquid/air interface. Unfortunately, we did not succeed in studying breakdown near the solid (hydrophobic or hydrophilic) surfaces. To show that objections on the grounds of possible contribution of contaminations to the breakdown probability can be ruled out, this design of the cuvette was also used to study breakdown in water and aqueous solutions containing added particles that absorb laser radiation, as well as in degassed water.

The measurable entity in all the experiments was the cavitation probability $w = n_0/n$, where n_0 is the number of pulses that caused cavitation and n is the total number of laser shots. The procedure guaranteed that a sporadic character for laser stimulation of cavitation (breakdown) would be retained. In all cases w was determined in a series of 10 experiments. Each series comprised 100 shots at a fixed temperature (i.e. $n = 100$).

B. Solution and Surface Preparation. Stock solutions (2 M) of four 1:1 inorganic electrolytes (KCl, KBr, NH_4Cl , and CH_3COONa) were prepared in water. The salts were of analytical reagent quality, and of purity greater than 99 or 99.5%. Before measurements, the stock electrolyte solutions were diluted to prepare solutions of five concentrations in the range from 0.05 to 1 M. Water was doubly distilled, and the electrical conductivity of the bulk water was $2 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$, pH 6.5. The water–electrolyte solutions were always in equilibrium with the atmosphere, and hence they contained dissolved gas.

All glassware was cleaned in chromic acid and hydrogen peroxide, and rinsed thoroughly with doubly-distilled water. The glass plates for the optical cavitation cuvette were cleaned using the same technique and considered to be hydrophilic. For these, practically complete wetting of the plates by water was achieved. The plate surface was rendered hydrophobic through modification by reaction with dimethyldichlorosilane. The glass plates were exposed to the silane vapor for a period of 48 h in a dry desiccator. Under these conditions, the chemisorption of silane^{36–38} on the glass plates leads to the formation of strongly hydrophobic surfaces with advancing contact angles for water within the range of 92–97°. Experimentally, there was no measurable difference in the contact angle on methylated glass of a droplet of water and a droplet of a 1 M solution of KCl, KBr, or NH_4Cl . A small amount of CH_3COONa leads to a drastic decrease in contact angle on methylated glass down to 65–70°. Further change in concentration has no influence on contact angle. However, at about 1 M the contact angle appears to increase. This may be due to the second-layer adsorption of CH_3COO^- .

For simulating the possible influence of absorbing “impurities” on optical breakdown, we used carbon powder. The main size of the carbon particles was 1 μm . Suspensions of several concentrations were prepared by intermixing the carbon powder in water or electrolyte solutions.

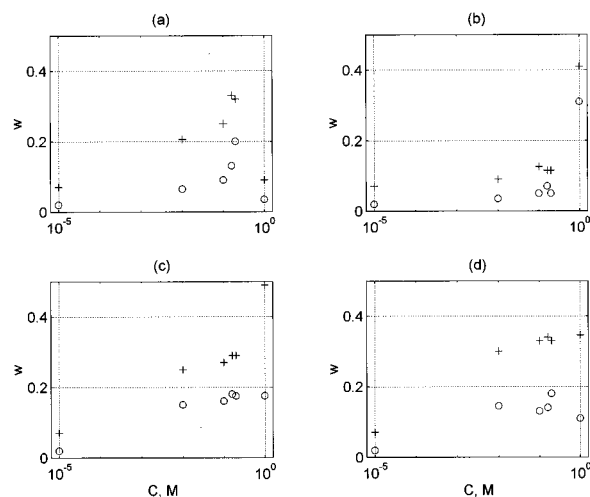


Figure 2. Optical cavitation probability w versus concentration of salt C for a thin layer of CH_3COONa (a), KBr (b), KCl (c), or NH_4Cl (d) confined between two hydrophobic (+) or two hydrophilic (O) surfaces. The leftmost points correspond to the case of pure water.

Doubly distilled water for some experiments on breakdown was degassed using a vacuum pump and a liquid N_2 cold trap. Before degassing, water was kept at the boiling point for a minimum of 1.5 h; then it was cooled quickly and submitted to 3 consecutive operations of freezing and melting at continuous degassing. With this arrangement, a vacuum of 10^{-3} Torr or better was obtained. Water was then sealed and injected into the cuvette. Care was taken not to introduce any air into the cuvette.

III. Results

A. Effect of Electrolytes. With the cuvette of the first design, experiments were carried out following the above scheme. The laser pulse intensity was an easily variable parameter in the experiments. It was prescribed so that the probability of cavitation for pure water at 20 °C in the cuvette with the hydrophilic surfaces, w_0 , would amount to about 0.02. In other words a base level situation was realized, in which about two laser pulses in a hundred would induce cavitation. This was attained when the intensity of the laser beam was about $I \sim 10^9 \text{ W/cm}^2$. At the same energy input, and under the same conditions, the probability of cavitation, w_1 , was then measured for hydrophobic surfaces. At the temperature 20 °C the ratio w_1/w_0 for pure water varied from about 3 to 4. Some scatter in the value of this ratio may be attributed to a number of difficult-to-control factors in each new series (e.g., methylation nonuniformity of the plate surface, fluctuation of the energy of the laser beam, etc.). We remark here that in a previous report¹⁸ we found that for pure water the value w_1/w_0 differs slightly from that in the present paper. That is because earlier we used slightly different conditions, i.e. a different laser pulse intensity, so that the value of w_0 for pure water was also different. Recall that the choice of the value of w_0 for pure water is arbitrary, it being important only that both w_1 and w_0 for all experimental conditions should be less than unity; i.e., the procedure should guarantee that a sporadic character for the laser stimulation is retained. Then, at the same energy input, and under the same focusing conditions, the probability of cavitation was measured for electrolytes of different concentration confined between hydrophobic or hydrophilic surfaces. The results for different 1:1 electrolytes at 20 °C are shown in Figure 2.

To finish this subsection, we have to note some further observations. The macroscopic air cavities had a size of the order of the cuvette thickness, i.e. about 10–20 μm .

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In the case of hydrophilic surfaces the three-phase contact line of the macroscopic bubbles has the shape of an ideal circle. If the size of a bubble thus formed is smaller than the interlayer thickness, then the bubble rapidly tears off from the wall and floats. For the cuvette with hydrophobic walls, the macroscopic cavity, independently of its size, continues to "stick" to the cuvette walls. The contact line slightly differs from a circular form. The shape of such a cavity depends on surface methylation nonuniformity.

B. Effect of Dissolved Gas. An observation made with cuvettes of the first design points strongly to a key role of dissolved gas in the optical cavitation phenomenon. This was true for all salts and all concentrations used. Namely, and we emphasize this, when the cavitation bubble tears off from the hydrophilic wall, laser shots made immediately after flotation of the macrobubble could not induce cavitation.

The effect of dissolved gas was studied with a cuvette of the second design. Remember that in this case we studied the probability of cavitation as a function of a distance from the air/water interface. The intensity of the laser beam in this experiment was about $I \sim 10^{10}$ W/cm². We found that changes in the breakdown probability as compared with the bulk case were observed only in a region that was less than 1 mm distant from the boundary with air. Unfortunately, we cannot define the value of this interval more precisely. If w_0 is the probability of breakdown in bulk water, then the probability w_1 near the interface with air turns out to be more than 10 times higher. The phenomenon cannot be related to a possible increase in concentration of dust particles (from the atmosphere) near the boundary with air. The influence of such absorbing radiation particles was simulated by adding carbon powder to the water and electrolyte solutions. In all the cases the breakdown probability was found to decrease abruptly with an increase in the suspension concentration. Clearly, the laser beam intensity becomes insufficient to stimulate breakdown. This is apparently connected with the absorption of radiation before the focal region, as well as with the thermal defocusing inside the focal neck.

A drastic decrease in breakdown probability was also observed for degassed water. It was found that no breakdown occurs in the degassed water within the range of the radiation intensities that give the sporadic character to the breakdown in water in contact with the atmosphere. To stimulate the first flashes in degassed water, it was necessary to increase the energy of the laser pulse 10 times as compared with that corresponding to the sporadic regime in the gassed water. In this case the pulse energy was about a 0.5 J! These observations are crucial. They confirm that the phenomenon is not due to impurities.

IV. Concluding Remarks

Thus, the results presented extend our earlier work.¹⁸ They show there is significant dependence of optical cavitation probability on electrolyte type, concentration, substrate, and presence of dissolved gas. We have previously interpreted the optical cavitation probability as a method for comparison of concentrations of submicrocavities.²⁷ If the original model for optical cavitation is correct, the present results could be interpreted in terms of submicrocavity structure. So, let us now list our main observations and try to give some (very tentative) analysis from the point of view of such a structure.

There is a conclusion, made first for the case of pure water, that it follows from our results can be generalized at least for 1:1 electrolytes. Namely, we found that for all salts and all concentrations the probability of cavitation in the case of hydrophobic surfaces is several times higher

than that in the case of hydrophilic surfaces. According to our model,^{18,27} this implies an increase in the concentration of gas-filled submicrocavities close to the hydrophobic wall or directly associated with it as compared with the hydrophilic case. We stress that in the present study we obtained additional evidence to favor the role of dissolved gas only, not impurities, in the cavitation phenomenon. The existence of such submicrocavities is in agreement with some observations made with some hydrophobic force measurements^{5,13,15,17} and slippage studies.¹⁹

There is also an important new observation that several 1:1 electrolytes give different values for the probability of cavitation, and even qualitatively different behavior. There is currently no theory that explains the adsorption of ions at the liquid/gas interface, or indeed at the oil/water or other (uncharged) interfaces.³⁹ The simple Onsager–Samaras approach⁴⁰ is a linear theory in which desorption of ions always occurs and is only very weakly ion specific. Nonetheless, surface charge vs pH observations,⁴¹ electrokinetic measurements,^{42–45} and thin-film studies^{46–49} allow one to conclude that the air/water interface is charged and that the charge is negative and likely due to OH[−] ions being in excess of H⁺ ions at the interface (Clearly HCO₃[−] ions from dissolved CO₂ can also participate in the charging process.⁵⁰ Whether these carbonic acid anions actually adsorb or simply enhance OH[−] adsorption remains unclear.) Moreover, the measured values of changes in interfacial tension with concentration at air/water interfaces^{34,35} depend critically on ion pairs. Thus, even for a planar interface, the Onsager theory often fails,^{34,35,41–44,46–49} a failure that can be traced to the assumption that the interactions of an ion with the liquid/gas interface are purely electrostatic in origin, apart from the linearization assumption and the very existence of the Hofmeister effect.³⁹ A completely neglected effect that gives rise to specificity of adsorption of ion pairs is dispersion interactions that dominate beyond 0.2 M concentration.⁵² If submicrocavities do exist, their very different geometry and scale can affect this ionic adsorption in a different way again. Hence it is not surprising that even within the same class of electrolyte, i.e. in our case several 1:1 electrolytes, adsorption differences can occur. These in turn could lead to the expectation of different submicrocavity ultrastructure of solution. This, which we believe, was reflected by our cavitation experiment (Figure 2).

One of our starting points was an experiment on macrobubble coalescence.¹⁶ However, we did not find any explicit correlation between our observations of optical

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cavitation and the experiment on macrobubble coalescence. This is likely due to the fact that the methylated glass surfaces used in the present work are fundamentally different in nature from the macroscopic bubbles.¹⁶ Presumably submicrobubbles may experience a different influence of salts as compared with the case of macrobubbles because of their much smaller size.

The above conclusion, however, does not exclude the fact that the methylated glass surface is similar to the liquid/gas interface. Actually, in both cases we found an enhanced probability of cavitation. In fact, other physical properties of the liquid/gas interface allow one sometimes to consider it as a very hydrophobic surface.

In summary, the experiments we have reported confirm an important qualitative role for dissolved gas and salt in determining the ultrastructure of aqueous solutions, in bulk and at interfaces. There is evidently a complex interplay between dissolved gas, electrolyte type, electrolyte concentration, and substrate. The role of dissolved

gas in liquid and solution structure has hardly begun to be considered theoretically in any depth and raises questions of some interest. In solid state physics the presence of impurity atoms or molecules and their association is a central issue. In liquids, dissolved gas molecules are present as such impurities at around 5×10^{-3} M, and it might be expected that they ought to have a similar role to play in setting ultrastructure.

Acknowledgment. This research was supported in part by a grant from the Japan–Former Soviet Union Scientist Collaboration Program of the Japan Society for the Promotion of Science (JSPS) and in part by Grant Nos. 96-03-32147 and 96-02-17236 from the Russian Foundation for Basic Research (RFBR). The authors are very grateful to K. Kurihara for support and for discussions which led to this work.

LA960265K