Amplification of the second-generation phonons in highly photoexcited CdS

1992 J. Phys.: Condens. Matter 4 9987

(http://iopscience.iop.org/0953-8984/4/49/025)

J. Phys.: Condens. Matter 4 (1992) 9987–9994. Printed in the UK

Amplification of the second-generation phonons in highly photoexcited CdS

S Juršėnas†, A Žukauskas† and R Baltramiejūnas‡

† Department of Physics, Vilnius University, Naugarduko g.24, Vilnius-2006, Lithuania
‡ Institute of Physics, Goštauto g.12, Vilnius-2600, Lithuania

Received 15 June 1992, in final form 2 September 1992

Abstract. The energy relaxation of a photogenerated electron–hole plasma is investigated in highly excited CdS at room temperature using time-resolved luminescence in the picosecond regime. It is established that the non-equilibrium carrier excess energy dissipation process exhibits a two-stage pattern with increasing excitation density. These stages reflect the sequential process of anharmonic decay of the non-equilibrium phonon system generated during plasma cooling. Experimental data are explained in terms of the kinetic model, taking into account two generations of non-equilibrium phonons. A high excitation level is shown to be a crucial condition for the manifestation of a second-generation phonon bottleneck in hot-carrier energy relaxation.

1. Introduction

Investigation of the thermalization of a photogenerated hot electron–hole plasma (EHP) in semiconductors is of great interest [1, 2]. It gives information about the fundamental interaction processes taking place in a dense system of non-equilibrium carriers (NCs) and phonons. At high laser excitation levels the momentum and the energy conservation in dissipation processes causes the accumulation of excess energy in limited ensembles of non-equilibrium quasiparticles. The slowing effect of the EHP cooling rate appears under such conditions [1], and the bottleneck in NC excess energy transfer to the lattice is caused by the system of non-equilibrium phonons. This system, generated during the plasma cooling, is located in a small region of k-space and mutually causes phonon reabsorption by the plasma reducing the EHP cooling rate.

In this paper the EHP cooling kinetics in the direct-gap semiconductor CdS have been studied by measuring time-resolved luminescence spectra. A new phenomenon is observed: the onset of two-stage energy relaxation with increasing excitation density, which is explained in terms of a model of depopulation of the non-equilibrium phonons of two generations.

2. Experimental details

Time-resolved measurements were performed using an experimental arrangement consisting of a passively mode-locked YAG:Nd^{3+} laser (pulse duration, about 30 ps)

0953-8984/92/499987+08$07.50

and a computer-controlled luminescence spectrometer. The temporal resolution was provided by means of a CS_2 optical Kerr shutter. The luminescence spectra were recorded photoelectrically by digital accumulation of the signal at each point, with discrimination of the pulses of unsuitable energy (the stability of excitation within 20% was preserved). The third harmonic of the laser ($h\nu_L = 3.5$ eV) was used for the excitation. The measurements were carried out at room temperature ($T_L = 298$ K).

3. Results and discussion

Figure 1 presents some typical time-resolved luminescence spectra of CdS crystals for two excitation intensities: $L = 600$ MW cm^{-2} and $L = 50$ MW cm^{-2}. The dominant emission band under such experimental conditions (high temperature and high excitation level) is due to dense EHP radiative recombination [3, 4]. The high-energy wing ($h\nu > E_g + k_B T_C + \Gamma$, where E_g is the band gap and Γ the collision broadening) of the EHP luminescence, shaped by the NC distribution function, reflects the effective carrier temperature for any delay time: $T_C(t) = -[\![k_B \partial\{\ln[I_{LUM}(h\nu, t)]\}/\partial(h\nu)]\!]^{-1}$ [5, 6]. This is confirmed by room-temperature experiments, where the plasma is excited resonantly (i.e. without excess energy), so that the high-energy wing reflects the lattice temperature fairly well [6]. Apparently, the enhancement of the high-energy tail of the plasma band due to multi-particle collision broadening [2, 7] is less significant for the room-temperature experiments. Figure 2 (open circles and open squares) depicts the time evolution of the plasma overheating $\Delta T_C(t) = T_C(t) - T_L$ at two excitation densities. One can see that a large part of the initial overheating decays rapidly during the first 50 ps, repeating the pump pulse. However, with increasing excitation density, the second slow stage of plasma cooling is clearly distinguished. It can be described by an exponential relationship $\Delta T_C(t) = \Delta T_C$ (60 ps) $\exp(-t/\tau_{II})$ with corresponding time constant τ_{II} equal to 320 ps for $L = 600$ MW cm^{-2}. Note that no trivial heating of the crystal lattice is manifest either in the first (fast) stage or in the second (slow) stage of EHP cooling. Such a heating would give a red shift to the EHP luminescence band of 0.13 eV for $\Delta T_L = 300$ K, but no shift is observed experimentally (figure 1).

The decrease in the temperature equalization rate of EHP and the crystal lattice may be caused by the slowing of energy exchange at different stages of the conversion of kinetic energy of NCs to heat (the latter means the increase in the phonon system energy in terms of a Planck distribution). Such a conversion is a chain of processes (figure 3) including the scattering of photoexcited NCs with high excess energy, amplification of first-generation non-equilibrium phonons via electron (hole)–phonon interaction, anharmonic decay of first-generation phonons to lower-frequency phonons, and the establishment of a Planck distribution in the crystal vibration system via phonon–phonon interactions. Obviously, the initial thermalization processes (the slowing of fast electrons in the plasma due to electron–electron scattering, and the establishment of an effective temperature T_C) occur on a short time scale (10^{-14}–10^{-12} s), i.e. below the time resolution of our equipment. The second stage of energy relaxation is determined by NC–phonon scattering processes. The rate of such processes can be reduced in a highly excited semiconductor by the screening of electron–phonon interactions. The influence of the screening effect was greatly exaggerated in earlier studies owing to the crude approximation proposed in [8]. Careful calculation shows that, for NC concentrations of about 10^{19} cm^{-3}, screening

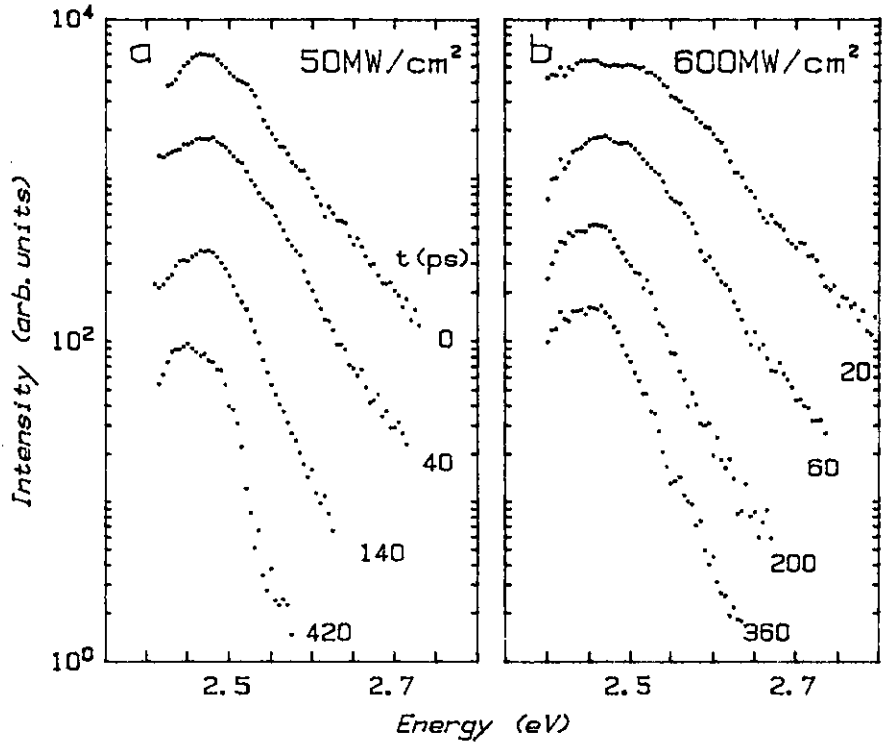

Figure 1. Time-resolved luminescence spectra of CdS crystals (T_L = 298 K) for (*a*) L = 50 MW cm^{-2} and (*b*) L = 600 MW cm^{-2} at different delays with respect to the pump pulse (the delay time in picoseconds is indicated by each spectrum).

could slow the plasma cooling in direct-gap semiconductors to 1 ps but cannot explain an energy relaxation time of about 100 ps [9].

The slowing of EHP energy relaxation due to the accumulation of non-equilibrium phonons directly interacting with NCS [10] should also be considered. The rate of such a process obviously is determined by the relaxation of the equivalent temperature (T_1) of non-equilibrium phonons, with a time constant equal, at elevated temperatures ($T_1 > \hbar\omega_0/k_B$), to the depopulation time τ_1' of LO phonons. For A^2B^6 crystals at room temperature this is about 1 ps [6, 11].

It follows that both the screening of electron–phonon interactions and the amplification of LO phonons under our experimental conditions can increase the plasma energy relaxation time to a few picoseconds. Apparently, these processes govern the cooling kinetics of the electron system in the first stage of energy relaxation, characterized by a time constant τ_I, probably less than the laser pulse duration τ_L.

Meanwhile, the second (slow) energy relaxation stage, occurring with increasing excitation density, is caused by other physical processes. In [12, 13] the slow EHP cooling kinetics were explained by a model of accumulation of the second-generation phonons, which are the products of the anharmonic decay of non-equilibrium LO phonons.

Until now, while analysing the energy transfer processes related to the cooling of

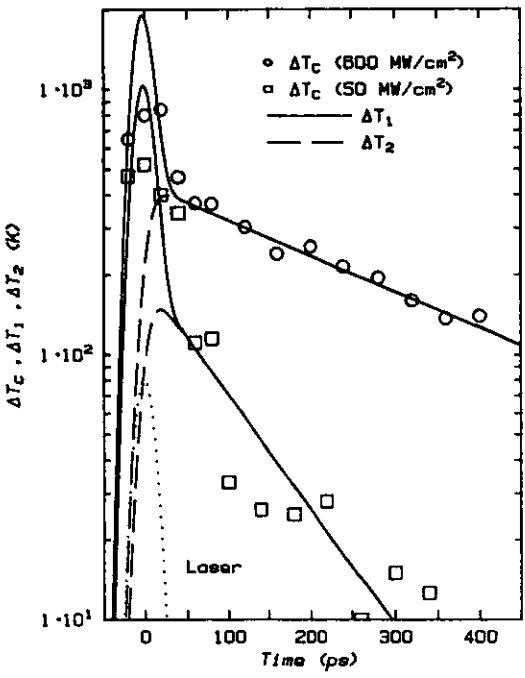

Figure 2. Kinetics of overheating of NCs and phonons in CdS crystals for $L = 50$ MW cm^{-2} and $L = 600$ MW cm^{-2}: O, □, experiment; ——, calculation of first-generation-phonon overheating; – – –, calculation of second-generation-phonon overheating; ·····, pump pulse.

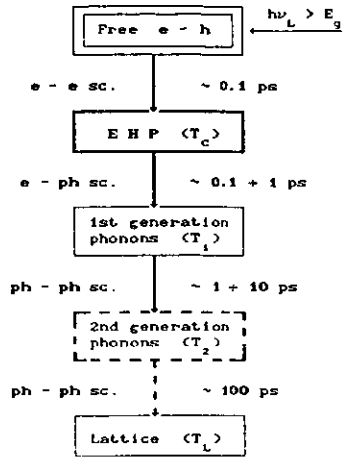

Figure 3. Diagram of the excess energy transfer to the lattice in a highly excited direct-gap one-valley semiconductor: e, electron; h, hole; ph, phonon; sc, scattering.

hot plasma, it was considered that the relaxation of the non-equilibrium population of optical phonons led directly to lattice heating [1]. According to the momentum conservation rule, an optical phonon with frequency ω_0 and wavevector q decays by a three-phonon anharmonic process [14] into two phonons of lower frequencies with wavevectors Q_1 and Q_2, where $|Q_1 - Q_2| \leqslant |q|$ [15] (an example of the anharmonic decay of non-equilibrium LO phonons in CdS crystals is shown in figure 4). This means that the products of long-wave LO phonon decay accumulate in a quasi-spherical layer of k-space with thickness $|q|$ and radius $|Q_0|$ (Q_0 is the average wavevector of subharmonic lattice vibration with frequency $\frac{1}{2}\omega_0$). If q is considerably less than the size of the first Brillouin zone (i.e. the typical situation in direct-gap semiconductors), then the increase in the second-generation-phonon temperature may considerably exceed the lattice heating, calculated using the equilibrium thermal heat capacity. If we take into account a phonon lifetime closely proportional to ω^{-5} [14], the second-generation non-equilibrium phonons with the approximate frequency $\frac{1}{2}\omega_0$ are able to slow considerably the process of EHP energy relaxation.

The possibility of accumulating the products of optical phonons in narrow intervals of frequency and wavenumber is experimentally confirmed. The observations of a non-equilibrium population of short-wave optical phonons near the frequency $\frac{1}{2}\omega_0$ at the coherent excitation of diamond [16] and of GaP [11] has been reported. Moreover, the accumulation of non-equilibrium low-frequency phonons in a narrow k-space

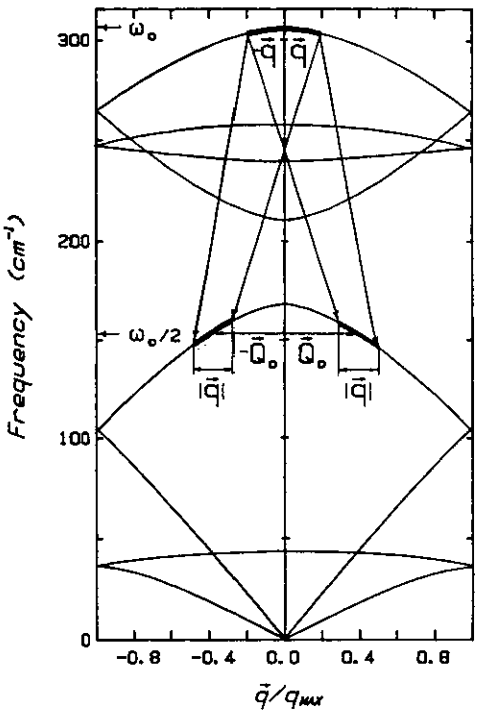

Figure 4. The phonon dispersion of a CdS crystal in the direction [001] [21]. The anharmonic decay of long-wave LO phonons is shown by arrows.

region in photoexcited semiconductors has been observed by means of a long-lived-phonon transport technique [17], second-order Raman spectroscopy [18] and diffusive x-ray scattering [19].

In order to verify this model, let us compare the experimental cooling kinetics of the EHP with the time evolution calculations of the occupation numbers of non-equilibrium phonons of the two generations. Assume that the effective plasma temperature on the time scale exceeding an electron–phonon coupling constant greater than 100 fs [1] is approximately equal to the equivalent temperature T_1 of long-wave LO phonons. The excess energy of the fast carriers is assumed to be transferred instantly to the first-generation non-equilibrium phonons. In order to simplify the problem, we introduce the occupation number $N_1(=[\exp(\hbar\omega_0/k_BT_1)-1]^{-1})$ of first-generation non-equilibrium phonons and the occupation number $N_2(=[\exp(\hbar\omega_0/2k_BT_2)-1]^{-1})$ of second-generation non-equilibrium phonons averaged in certain regions of k-space. In such an approximation, the time evolution of N_1 and N_2 can be calculated by solving the following system of kinetic equations:

$$dN_1/dt = I_L(t)(h\nu_L - E_g)/d\hbar\omega_0\rho_1 - [N_1(N_2+1)^2 - (N_1+1)N_2^2]/\tau_1 \qquad (1)$$

$$dN_2/dt = (2\rho_1/\rho_2)[N_1(N_2+1)^2 - (N_1+1)N_2^2]/\tau_1 - (N_2 - N_2^0)/\tau_2. \qquad (2)$$

Here ρ_1 and ρ_2 are the effective densities of the modes of first- and second-generation non-equilibrium phonons, respectively, $h\nu_L - E_g$ is the excess energy of photoexcitation, $I_L(t)$ is the excitation intensity and d is the excited crystal thickness. The time constant τ_2 reflects the rate of the relaxation of non-equilibrium occupation to the equilibrium value N_2^0 for the phonons with frequency $\frac{1}{2}\omega_0$, and τ_1 is the lifetime of LO phonons at $T_L = 0$ K.

The number of first-generation phonon modes active in the energy transfer is approximated by the volume of a sphere centred at $k = 0$. The radius of the sphere is determined by the characteristic wavenumber of LO phonons, emitted by the heaviest carriers, namely holes: $q_h = (2m_h\omega_0/\hbar)^{1/2}$. Thus,

$$\rho_1 = [1/(2\pi)^3]\tfrac{4}{3}\pi q_h^3. \tag{3}$$

In a quasi-spherical layer of k-space, where the products of non-equilibrium LO-phonon decay accumulate, the density of modes for $q_h \ll Q_0$ is

$$\rho_2 = [1/(2\pi)^3]4\pi Q_0^2 q_h. \tag{4}$$

The exciting photon flux density has a Gaussian time profile

$$I_L(t) = (2.72/\pi)^{1/2}(L/h\nu_L)\exp(-2.72t^2/\tau_L^2) \tag{5}$$

where L is the density of the laser beam power and τ_L is the full width at the half-magnitude of the pulse (25 ps).

In such an approximation, the first term on the right-hand side of equation (1) reflects the increase in the LO-phonon occupation number due to the energy relaxation of hot NCS. The second term is the full relaxation rate of the non-equilibrium occupation of first-generation phonons, including annihilation of two second-generation non-equilibrium phonons to give an LO phonon [20]. The first term on the right-hand side of equation (2) is the full rate of the increase in the occupation number of second-generation non-equilibrium phonons. The multiplier 2 means that a decay of one LO phonon produces two subharmonic phonons. The second term is the full relaxation rate of the non-equilibrium occupation of the second-generation phonons. The relaxation time τ_2 contains a contribution from the anharmonic lifetime of subharmonic phonons and from the time of diffusion of such phonons from the excited 'hot' region of the crystal. The diffusion of the first-generation LO phonons located near $k = 0$ can be neglected because of their zero group velocity.

The system of equations (1)–(5) was solved numerically, using the following parameters for CdS: $E_g = 2.46$ eV; $\hbar\omega_0 = 38$ meV; $m_h = 1.14m_0$ (averaged in all directions). The value of Q_0 is the average wavenumber of $\frac{1}{2}\omega_0$ phonons (in these crystals they belong to the B_1 branch): 1×10^8 cm^{-1} [21]. The values of $\tau_2 = 320$ ps and $\tau_2 = 100$ ps were taken from experiment (τ_{II}). The fitting parameters were d and τ_1. The best coincidence of the experimental value of T_C with the calculated equivalent phonon temperature T_1 for $L = 600$ MW cm^{-2} was found at $d = 1.6$ μm and $\tau_1 = 2$ ps, and for $L = 50$ MW cm^{-2} at $d = 0.3$ μm and $\tau_1 = 2$ ps.

As seen from figure 2, the proposed model is able to describe quantitatively the occurrence of two stages of plasma temperature relaxation in highly excited crystals of CdS. Figure 2 also depicts the temporal evolution of the equivalent temperature of the second-generation non-equilibrium phonons (broken curve). The striking feature of the calculated kinetics is the equalization of equivalent temperatures T_1 and T_2 at the beginning of the slow stage of energy relaxation, showing the hindering of plasma cooling by the second-generation non-equilibrium phonons.

It should be noted that the values of the fitting parameters τ_1 agree with the lifetime of LO phonons (10 ps or less) in compound semiconductors. However, the second adjustable parameter, namely the thickness of the excited crystal d,

considerably exceeds the traditional absorption depth α^{-1} (of about 0.1 μm) in which the NC excess energy is dissipated [6]. This situation is typical for high-excitation-level experiments [22]. The excited depth is enhanced because of the probable effects of self-induced transmission and light reabsorption. The enhancement of the excited depth in our experiment is evidenced by a disproportionately small increase in the peak of the EHP excess temperature from $\Delta T_C(20\ \text{ps}) = 520$ K to 830 K with increasing excitation density from 50 to 600 MW cm^{-2}. The same can be said about the initial plasma density (obtained from the spectral analysis) increase from $n(20\ \text{ps}) = 1 \times 10^{19}$ cm^{-3} to 2×10^{19} cm^{-3}. So, at low excitation levels the system of non-equilibrium phonons is created in a narrow excited region of about 0.1 μm. It is expected that some second-generation non-equilibrium phonons are able to leave the excited region before the anharmonic decay (taking into account the group velocity $v_g = 400$ m s^{-1} of such phonons (see figure 4)). With increasing excitation density, the thickness of the excited region is enhanced, and the fraction of diffused phonons decreases. In such conditions, τ_2 depends on the excitation density. At a high excitation density ($L = 600$ MW cm^{-2}), when the excited depth $d > 1$ μm considerably exceeds the free path of non-equilibrium phonons, one may suppose that the depopulation time τ_2 is determined essentially by the anharmonic lifetime of the second-generation phonons.

A high excitation level is clearly an important condition for the manifestation of the slow stage of plasma cooling. This allows first the creation of a dense population of non-equilibrium phonons and second the enhancement of the excitation depth above the free path of the second-generation non-equilibrium phonons. An energy relaxation bottleneck due to the second-generation phonons has also been observed under steady-state excitation in GaAs–$Ga_{1-x}Al_xAs$ microstructures, probably because of the trapping of the phonons in the light-absorbing layers [23].

4. Conclusions

This paper demonstrates the possibility of reducing the rate of plasma cooling during the slow relaxation stage by the second-generation non-equilibrium phonons produced at high excitation densities. The heating of such phonons is most marked when the wavenumbers of the first-generation non-equilibrium phonons (LO phonons) are small and their decay excites a narrow region of k-space. Apparently, such a situation is typical for direct-gap one-valley semiconductors where, during the energy relaxation process, only long-wave optical phonons are created initially.

References

[1] Lyon S A 1986 *J. Lumin.* **35** 121
[2] Rühle W W, Collet J, Pugnet M and Leo K 1991 *Condensed Systems of Low Dimensionality* ed J L Beeby *et al* (New York: Plenum) p 61
[3] Lysenko V G, Revenko V I, Tratas T G and Timofeev V V 1975 *Zh. Eksp. Teor. Fiz.* **68** 335 (Engl. Transl. 1975 *Sov. Phys.–JETP* **41** 163)
[4] Saito H, Hayashi M and Shionoya S 1977 *Solid State Commun.* **24** 837
[5] Shah J 1978 *Solid State Commun.* **21** 43
[6] Baltramiejūnas R, Žukauskas A and Tamulaitis G 1986 *Zh. Eksp. Teor. Fiz.* **91** 1909 (Engl. Transl. 1986 *Sov. Phys.–JETP* **64** 1132)
[7] Collet J H, Rühle W W, Pugnet M, Leo K and Million A 1989 *Phys. Rev.* B **40** 12296

[8] Yoffa E J 1981 *Phys. Rev.* B **23** 1909
[9] Das Sarma S, Jain J K and Jalambert R 1988 *Solid State Electron.* **91** 695
[10] Kocevar P 1972 *J. Phys. C: Solid State Phys.* **5** 3349
[11] Rhee B K and Bron W E 1986 *Phys. Rev.* B **34** 7107
[12] Baltramiejūnas R, Žukauskas A, Latinis V and Juršėnas S 1987 *Pis. Zh. Eksp. Teor. Fiz.* **46** 67 (Engl. Transl. 1987 *JETP Lett.* **10** 511)
[13] Baltramiejūnas R and Žukauskas A 1988 *Phys. Status Solidi* b **149** 337
[14] Klemens P G 1966 *Phys. Rev.* **148** 845
[15] Levinson Y B 1986 *Nonequilibrium Phonons in Nonmetallic Crystals* ed W Eisenmenger and A A Kaplyanskii (Amsterdam: North-Holland) p 91
[16] Colles M J and Giordmaine J A 1971 *Phys. Rev. Lett.* **27** 670
[17] Ulbrich R G, Narayanamurti V and Chin M A 1980 *Phys. Rev. Lett.* **45** 1432
[18] Tsen K T, Abramsohn D A and Bray R 1982 *Phys. Rev.* B **26** 4770
[19] McWhan D B, Hu P, Chin M A and Narayanamurti V 1982 *Phys. Rev.* B **26** 4774
[20] Ferry D K 1974 *Phys. Rev.* B **9** 4277
[21] Nusimovici M A, Balkanski M and Birman J L 1970 *Phys. Rev.* B **1** 595
[22] Majumder F A, Swoboda H-E, Kempf K and Klingshirn C 1985 *Phys. Rev.* B **32** 2407
[23] Weinert H, Žukauskas A, Latinis V and Stepankevičius V 1988 *Pis. Zh. Eksp. Teor. Fiz.* **47** 340 (Engl. Transl. 1988 *JETP Lett.* **47** 407)