Spectrum of depolarized molecular light scattering near the critical solution stratification temperature

V. F. Kitaeva, G. I. Kolesnikov, N. N. Sobolev, V. S. Starunov, I. L. Fabelinskiĭ, and V. Ya. Shreĭner

P. N. Lebedev Physics Institute, Academy of Sciences, USSR

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Strong narrowing of the Rayleigh line wing (RLW) is observed on approach to the critical phase separation temperature in an aniline-cyclohexane solution. A three-pass Fabry-Perot interferometer with a spectrum resolution 10^8 is employed and photon counting is used for the recording. Indications are obtained that the RLW narrowing is nonmonotonic. In the $T-T_c$ temperature range between 25 and 0.4 °C the RLW narrows by 5–6 times.

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INTRODUCTION

The depolarized Rayleigh line wing (RLW), arising as a consequence of light scattering on anisotropy fluctuations, has long been successfully used in the study of the orientational motion of molecules in fluid media.[1] Relatively recently, a series of experiments was done related to the study of the RLW in mixtures near the critical stratification point. In the first of these works,[2] in the study of the nitrobenzene—*n*-hexane solution, a strong narrowing of the RLW was observed on approach to the critical stratification temperature, T_c, from the side of the homogeneous phase. Under these same conditions a strong narrowing of the RLW was observed in solutions of *n*-dodecane—β, β' dichlorodiethyl ether,[3] carbon disulfide—ethanol[4], and *n*-hexadecane–β, β' dichlorodiethyl ether.[5] In all of the above mentioned solutions a nonmonotonic narrowing of the RLW was observed: temperature intervals in which the width of the RLW is almost constant alternated with temperature intervals where the width of the RLW changed very rapidly. Two or three temperature regions of strong variation of the RLW were observed, but in the carbon disulfide–ethanol solution only one such region was observed.[4]

Meanwhile, other authors were unable to observe the strong narrowing of the RLW in solutions of nitrobenzene–*n*-hexane[6–8] and nitroethane–3-methylpentane,[9] and they deny the existence of RLW narrowing. Thus, there exists a discrepancy among the experimental data of different authors even for one and the same solution.

Originally it was assumed[6] that our[2] observed narrowing of the RLW in a nitrobenzene–*n*-hexane solution is an illusory effect, arising as a consequence of the superposition of a central line, intense near T_c and depolarized as a consequence of multiple scattering at critical opalescence, on the studied spectal range of spikes. However, it was later ascertained[3,7,10] that just near T_c the widths of the RLW is the nitrobenzene–*n*-hexane solution the RLW widths practically coincide in the studies of the authors who detected and did not detect the RLW narrowing.

The significantly different results of the measurements of the RLW width pertain to a temperature region far from T_c, where there is no effect of multiple scattering of the light. Authors who observed the narrowing of the RLW far from T_c found greater widths than authors who did not observe the narrowing. In the analysis of the causes of the noted discrepancy,[10] the necessity to allow for the complex nature of the spectral distribution of intensity in the Rayleigh line wing was indicated. In binary solutions this distribution is described by a sum of three or even more Lorentzians1):

$$I(\Omega)=\frac{C_0\Omega_0}{\Omega_0{}^2+\Omega^2}+\sum\frac{C_i\tau_i}{1+\Omega^2\tau_i{}^2}, \tag{1}$$

where $\tau_i>\tau_{i+1}$ are the relaxation times of the anisotropy, C_i are the weights of the corresponding Lorentzians, Ω_0 and C_0 are the width and weight of the Lorentzian arising as a consequence of light scattering by fluctuations of concentration of light depolarized, as mentioned above, as a consequence of multiple scattering. Recognizing that near T_c, $C_0\gg C_i$ and as a rule, $C_{i+1}\ll C_i$, it is easy to understand the complexity of the problem of obtaining data about τ_i from the observed contour of the RLW.

Below we will again return to the discussion of possible causes of the discrepancy between the results of experiments by different authors. Right here we note that according to recently published[4] measurements of depolarized lines of Raman scattering of light (LRSL), on the width of which multiple scattering has no effect, one can conclude that there is satisfactory correlation between the narrowing of the RLW and the narrowing of depolarized LRSL in solutions upon approach to T_c. This seems natural, since the width of the RLW and a significant fraction of the width of LRSL are dependent upon one and the same physical process.[11]

In the present work the spectrum of the RLW was studied in a solution of aniline–cyclohexane upon approach to T_c. It was done using a three-pass Fabry-Perot interferometer which made it possible to almost completely eliminated the effect of multiple scattering on the widths of studied sections of the RLW.

1. EXPERIMENTAL PROCEDURE

Experimental apparatus

The experimental apparatus is shown schematically in Fig. 1. As the source of exciting light a single frequency

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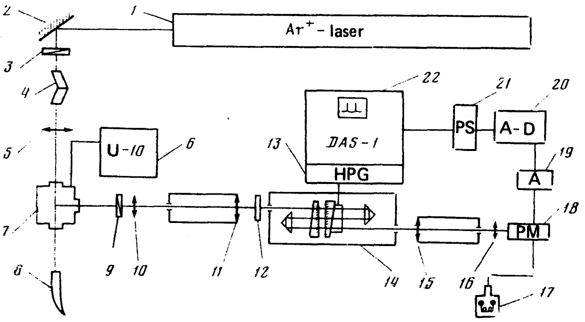

FIG. 1. Schematic of the experimental apparatus: 1—laser; 2—turning mirror; 3, 9—polarizers; 4—Fresnel rhombus; 5, 10, 11, 15, 16—objectives; 6—thermostat; 7—chamber with the fluid under study; 8—Wood's horn; 12—interference filter; 13—high voltage generator (HVG); 14—three-pass Fabry-Perot interferometer; 17—Dewar vessel; 18—photomultiplier; 19—preamp; 20—amplifier-discriminator; 21—pulse shaper; 22—DAS-1 system.

argon laser (Spectra Physics model 171-03, $\lambda = 514.5$ or 476.5 μm) was used. The laser radiated with a power of 50–70 mW, polarized in the scattering plane. It was focused by a lens, 5, into the cell, 7, which contained the solution under study. The spectrum of the depolarized light, scattered through an angle $\vartheta = 90°$, was analyzed with the aid of a stabilized three-pass Fabry-Perot piezoelectric scanning interferometer manufactured by Burleigh. The interferometer had a resolution of $\sim 10^8$ and finesse ~70. An interference filter, 12, with a transmission band width ~40 cm^{-1} was placed in front of the interferometer to remove light due to Raman scattering.

The scattered light was recorded by a cooled photomultiplier, 18, (EMI ± 9558B) with magnetic defocusing, which operated in the regime of photon counting. The dark current of the PM consisted of 1–2 photo-pulses per second. The signal of the PM was registered by a Berleigh DAS-1 instrument, which combined a 1024-channel spectrum analyzer with a logic circuit that maintained constant the parrallelism of the interferometer plates.

One order of the interferogram was recorded in 680 channels of the spectrum analyzer. The result of the accumulation was computed every 5–10 channels. A large portion of the measurement was accomplished with interferometer free spectral ranges, 13.2, 11, 8.6, and 4.2 cm^{-1}.

The design of the chamber with the solution under study made it possible to vary the temperature of the solution and maintain temperature uniformity in the cell to within ±0.5 °C.

The aniline–cyclohexane solution had a critical concentration of 0.51 molar fraction of analine and a critical stratification temperature 31.4 °C. After the temperature was stabilized, the solution was vigorously agitated several times and then again was maintained at the same temperature until the spectrum began to be recorded. The spectrum was then recorded after a three-hour delay for temperatures far from T_c and after 4–5 hours for temperatures near T_c. The spectrum of the scattered light was recorded at each temperature no less than three times, and then the results of the spectrum reduction (the procedure for which is described below) were averaged.

B. Spectrum reduction procedure

The great resolution and finesse in our experiment significantly simplified the analysis procedure for the obtained spectra. As a rule, the halfwidth of the apparatus function was 5–10 times narrower than the halfwidth of the studied region of the RLW. On the basis of a calculation[12] this means that the actual halfwidth of the RLW will differ from the observed halfwidth by only a few percent. On the other hand, the accuracy of measuring the observed halfwidth of the RLW was ~10–15%. Therefore it was unnecessary to introduce a correction for the finite but small width of the apparatus contour.

More difficulties are often encountered in the allowance for the effect exerted on the RLW spectrum by the tails of the intense light of multiple scattering by the concentration fluctuations (the first term in Eq. (1)).

The large resolution in the spectrum allowed the study of RLW undistorted by the effect of multiple scattering at frequencies exceeding 4–5 halfwidths of the apparatus contour. For illustration, Fig. 2 shows the frequency distribution (number of pulses, P) obtained at temperatues exceeding the critical temperature by $\Delta T_c = 2.9°$ (circles, curve 1) and by $\Delta T_c = 0.6°$ (triangles, curve 2), and the apparatus contour of the experimental setup (curve 3). The frequency is measured from the frequency of the exciting light. At maximum intensity the number of pulses, P, is: for curve 1 – $P_{max} = 2.1 \times 10^2$ pulses, for curve 2 – $P_{max} = 2.4 \times 10^3$ pulses, for curve 3 – $P_{max} = 2.0 \times 10^3$ pulses.

From this figure and the cited values of P_{max} for each curve it is evident that it is possible to analyze the RLW without taking into consideration multiple scattering for $\Delta T_c = 2.9°$ starting from $\Delta\nu = 0.3$ cm^{-1}, and for $\Delta T_c = 0.6°$ starting from $\Delta\nu = 0.4$–0.5 cm^{-1}. This is exactly what we did. In this way, our results are not burdened by errors due to the effect of multiple scattering on the intensity distribution in the RLW.

In the reduction of the interferogram another question arises, namely, identification of the level for which the intensity of the RLW should be measured. One can examine two extreme cases.

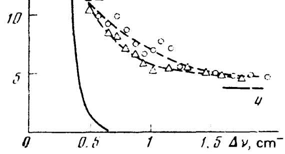

FIG. 2. Number of pulses, P, of the scattered light vs. frequency $\Delta\nu$ 1—$\Delta T_c = 2.9°$; 2—$\Delta T_c = 0.6°$; 3—contour of the apparatus function; 4—reference level of the intensity of the scattered light. The free spectral range of the interferometer is $[\Delta\nu] = 8.62$ cm^{-1}.

If the width of one of the Lorentzians in Eq. (1), for example $\delta\nu_3$, is significantly greater than the interferometer free spectral range $[\Delta\nu]$, and the widths of the remaining Lorentzians, $\delta\nu_1$ and $\delta\nu_2$, are significantly less than $[\Delta\nu]$, then the intensity of the RLW should be reckoned from the level $I_{\min}$ of the intensity in the midpoint between neighboring maxima of the interferogram, and the obtained contour should be treated as a sum of several Lorentzians. If, as before, $\delta\nu_1$ and $\delta\nu_2 \ll [\Delta\nu]$, and $\delta\nu_3$, although less than the free spectral range, is comparable with it, so that of the contours of this Lorentzian form neighboring orders overlap, then the intensity of the RLW should be reckoned from the level $\frac{1}{2}I_{\min}$ (Ref. 1).

We assume that in our case, the results obtained by reckoning the intensity of the RLW from the level $I_{\min}$ correspond much closer to the correct results. As a basis for this assumption is the fact that when decreasing $[\Delta\nu]$ from 13 to 4 cm^{-1} and decreasing ΔT_c from 25 to 0.6°, the quantity $I_{\min}$, within experimental error, does not vary.

Measuring the intensity of the RLW from $\frac{1}{2}I_{\min}$ or from $I_{\min}$, we then plotted I^{-1} vs $\Delta\nu^2$. If the intensity distribution in the RLW is described by a sum of several Lorentzians (Eq. (1)) with not very close values of τ_i, then there should be observed on the graph of I^{-1} vs $\Delta\nu^2$ just as many linear regions. For example, Fig. 3 shows the variation of I^{-1} vs $\Delta\nu^2$ for the aniline-cyclohexane solution at $\Delta T_c = 9°$, for $[\Delta\nu] = 9.3\ \text{cm}^{-1}$ and with the intensity reckoned from the level $I_{\min}$. The arrow notes the frequency, starting with which multiple scattering no longer contributes to the intensity distribution on the studied region of the RLW. In Fig. 3, there are clearly visible two linear regions corresponding to Lorentzians with halfwidths $\delta\nu \approx 0.3 - 0.4\ \text{cm}^{-1}$ and $\delta\nu \approx 0.9 - 1\ \text{cm}^{-1}$.

Figure 4 shows the variation of I^{-1} vs $\Delta\nu^2$ for $\Delta T_c = 0.6°$ (triangles) and $\Delta T_c = 2.9°$ (dots), constructed from the points on Fig. 2, with the intensity reckoned from the level $I_{\min}$. Since the signal level due to the RLW is very low and is rather strongly distorted by noise, as is evident from Fig. 4, it is not always possible to construct uniquely straight-line segments in the coordinates $I^{-1}(\Delta\nu^2)$.

Such a case is shown in Fig. 4 for $\Delta T_c = 2.9°$, where two lines 1′ and 1″ are drawn, corresponding to the possible largest and smallest slopes. From the slopes of these lines, the halfwidth values $\delta\nu = 0.61\ \text{cm}^{-1}$ and $\delta\nu = 0.73\ \text{cm}^{-1}$ are obtained. For $\Delta T_c = 0.6°$ (line 2) we find $\delta\nu = 0.31\ \text{cm}^{-1}$. Consequently, upon changing the temperature by 2.3° the width of the RLW in the studied region decreases by a factor of 2. We note that the viscosity in this temperature interval decreases only by 15%. It is thus shown also in this example, for two temperatures, that there is a strong narrowing of the RLW in the aniline-cyclohexane solution upon approach to T_c.

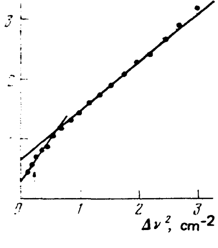

FIG. 3. Reciprocal of the intensity in the RLW $1/I$ vs. the square of the frequency $\Delta\nu^2$ for $\Delta T_c = 9°$ and $[\Delta\nu] = 9.3\ \text{cm}^{-1}$.

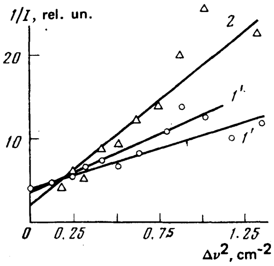

FIG. 4. Reciprocal of the intensity in the RLW $1/I$ vs. the square of the frequency $\Delta\nu^2$: 1′ and 1″ (dots)—$\Delta T_c = 2.9°$; 2 (triangles—$\Delta T_c = 0.6°$. The free spectral range of the interferometer is $[\Delta\nu]$ 8.62 cm^{-1}.

2. EXPERIMENTAL RESULTS

Measurements of the halfwidth, $\delta\nu$, of the RLW by the method described above permits the determination of the anisotropy relaxation time $\tau = (2\pi c\delta\nu)^{-1}$. The measurements were made in the critical aniline-cyclohexane solution in the temperature interval from $\Delta T_c = 25.6°$ to $\Delta T_c = 0.4°$. The dependence of $\ln(\tau \cdot 10^{12})$ on $\ln\varepsilon$ ($\varepsilon = \Delta T_c/T_c$, where T_c is the critical temperature in degrees Kelvin) is shown in Fig. 5.

In this figure are shown the results of the analyzed measurements in cases where the intensity of the RLW is measured from the level $I_{\min}$ (dots, curve 1) and when it is measured from the level $\frac{1}{2}I_{\min}$ (triangles, curve 2). As is evident from Fig. 5, the temperature dependence of the relaxation time does not depend on the reference level of the intensity of the RLW. Over the temperature range from $\Delta T_c = 9°$ to $\Delta T_c = 0.4–0.6°$, τ increases by 5–6 times; at the same time the shear viscosity, η, increases in the same range by only about one-half. The relaxation time on approach to T_c grows nonmonotonically: up to $\Delta T_c = 9°$ it increases slowly, approximately following the change in viscosity ($\tau \sim \eta$). In the tempera-

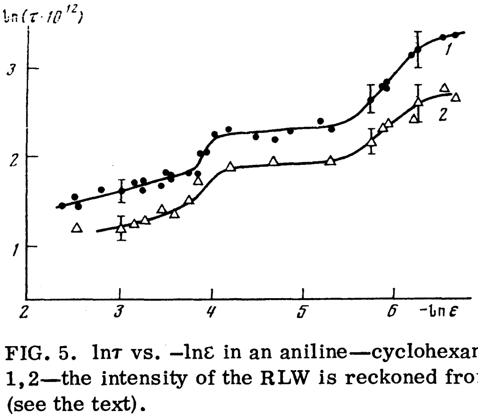

FIG. 5. lnτ vs. −lnε in an aniline—cyclohexane solution. 1,2—the intensity of the RLW is reckoned from different levels (see the text).

ture interval from $\Delta T_c \approx 7-9°$ to $\Delta T_c \approx 5.5°$, τ rapidly rises and then does not change right down to $\Delta T_c \approx 1.5-1°$. Beginning from $\Delta T_c \approx 1°$ and to $\Delta T_c \approx 0.6°$, τ again increases. The character of the temperature dependence of τ at $\Delta T_c < 0.6°$ remains unclear. From Fig. 5 one could draw the conclusion that at $\Delta T_c < 0.6°$, τ tends to a constant value. However, this conclusion turns out to be incorrect, since, as estimates show, near T_c, at the employed laser power, the scattering volume can be heated by several tens of degrees, and more the closer to T_c.

As was stated, there are experimental grounds for using the results of the measurements of $\delta\nu$ and τ obtained by reckoning the intensity of the RLW from the level $I_{\min}$ (curve 1 on Fig. 5). Therefore we will describe in somewhat greater detail the temperature kinetics of $\delta\nu$ and τ for this analysis procedure, although qualitatively the results remain the same for other analysis procedure.

Far from the critical temperature in the studied solution there are distinctly observed two regions of the RLW, corresponding to two Lorentzians with half widths $\delta\nu_1 \approx 0.3-0.4$ cm^{-1} and $\delta\nu_2 \approx 0.9-1$ cm^{-1}. At greater ΔT_c we traced the temperature variation of the Lorentzian with halfwidth $\delta\nu_2$.

From $\Delta T_c = 25°$ to $\Delta T_c \approx 7-9°$ the width of this region of the RLW varied slowly, approximately inversely proportional to the viscosity ($\tau_2 \sim \eta$). Beginning from $\Delta T_c \approx 7-9°$, $\delta\nu_2$ decreased very rapidly reaching the value ~0.55–0.6 cm^{-1} at $\Delta T_c = 5.5°$ and then remained roughly constant down to $\Delta T_c \approx 1.5°$. Upon decrease of ΔT_c from ~1.5 to 0.4°, the halfwidth of the RLW decreased rapidly from 0.55 to 0.18 cm^{-1}.

3. DISCUSSION OF THE RESULTS

In the aniline-cyclohexane solution upon changing the temperature from $\Delta T_c = 25$ to $\Delta T_c \approx 0.4°$, a narrowing of the RLW by approximately 6 times, from $\delta\nu \approx 1$ cm^{-1} to $\delta\nu \approx 0.18$ cm^{-1}, was observed. The narrowing bears a nonomonotonic character. Two temperature intervals are observed where the RLW narrows vary rapidly. From $\Delta T_c \approx 7-9°$ to $\Delta T_c \approx 5.5°$, $\delta\nu$ decreases from a value of ~1 cm^{-1} to ~0.55 cm^{-1}. Then down to $\Delta T_c \approx 1.5°$ no such marked change in the spectrum of the RLW occurs.

In the temperature interval from $\Delta T_c \approx 1.5$ to $\Delta T_c \approx 0.4°$ the RLW again rapidly narrows to $\delta\nu \approx 0.18$ cm^{-1}. The behavior of the RLW from $\Delta T_c \approx 0.4-0.6°$ still remains unclear.

At the present time two mechanisms were proposed to explain the RLW narrowing near T_c. In Chaban's[13] theory the cause of the narrowing of the RLW is considered to be the divergence of the concentration fluctuations upon approach to T_c. In this theory the expression for the free energy takes into account the product of the mean squared the anisotropy-tensor fluctuations and the mean square concentration fluctuations. In Chaban's theory expression of the form

$$\tau = (a + b\varepsilon^{\sigma})^{-1} \qquad (2)$$

is obtained for the anisotropy relaxation time, where a and b depend weakly on the temperature, and the parameter $\sigma = 0.8$. Equation (2) predicts a retardation of the growth of τ in the immediate vicinity of T_c. In this and in earlier works (Ref. 3–5), it was actually experimentally observed that for $\Delta T_c \approx 1$ to 0.6° the growth of τ is retarded or ceases. However, as was already pointed out, this retardation of the growth of τ can be a consequence of the heating of the medium at the employed laser power.

If the nonomonotonic temperature variation of τ is neglected, then by analyzing the experimental data using equation (2), the value $\sigma \approx 0.6-1$ is obtained. But if equation (2) is applied in the analysis for each of the temperature regions of the rapid growth of τ then, as before (Refs. 3–5), we get $\sigma \approx 2 \pm 0.5$.

Another mechanism of RLW narrowing upon approach to T_c was pointed out by Wilson.[14] According to Wilson, in the vicinity of T_c, the coefficient of rotational diffusion, D_r, can be expressed by the well known Stokes-Debye formula with substitution of the particle radius by the correlation radius r_c:

$$D_r = kT/8\pi\eta r_c^3. \qquad (3)$$

Since $\tau = (6D_r)^{-1}$ and $r_c \sim \varepsilon^{-0.63}$, we obtain $\tau \sim \varepsilon^{-\sigma}$, where $\sigma \approx 2$, which, within the limits of experimental error, is in agreement with the results obtained by analyzing each of the regions of the rapid growth of τ.[2)]

In the case of a molecule with a nonspherical shape it is necessary to take into account the differences in the values of the three main diffusion coefficients D_1, D_2, and D_3.

As was shown earlier,[15] in the case of a symmetric top molecule ($D_3 = D_2 < D_1$), the contour of the RLW is described by a sum of three Lorentizians with halfwidths $\delta\nu_1 = 6D_2$, $\delta\nu_2 = D_1 + 5D_2$, and $\delta\nu_3 = 4D_1 + 2D_2$. If we assume that Wilson is correct and that $D_r \to 0$ as $T \to T_c$, than at the critical point all $D_i \to 0$ and $\delta\nu_i \to 0$.

One can go further and propose that as $T \to T_c$ not all the principal values of the diffusion coefficient vanish at one and the same temperature. For example, if $D_1 = D_2$ vanish at some temperature far from T_c and then after another temperature interval D_3 also vanishes, then it is possible to select definite values of D_i, and consequently also $\delta\nu_i$, which describe the RLW narrowing pattern which we observed. It must be remembered however, that this is merely a hypothesis in need of experimental and theoretical investigation.

It is entirely possible that both of the mechanisms introduced by Chaban[13] and Wilson[14] play a role in the narrowing of the RLW. However, the presence of the RLW narrowing effect in solutions as $T \to T_c$ is not subject to doubt.

Possible causes inhibiting the observation of changes in the RLW were pointed out by us earlier.[10] Recently Beysens and Zalczer[8] again stated that in their experiments in a nitrobenzene-n-hexane solution as $T \to T_c$ the narrowing of the RLW is not observed, but on the other hand, the intensity of a narrow region of the RLW grows according to the law $I \sim \varepsilon^{-0.22}$, that is, the intensity of the scattered light increases when the temperature of the solution is decreased. This "strange" phenomenon, of course, was not explained in the cited work.[8] Yet is is easily and naturally explained if the effect of narrowing of a broader region of the RLW in the same solution is considered; we reported this narrowing earlier (Refs. 3 and 10). Studies of the temperature dynamics of the RLW in the present work and also in previous works (Refs. 2–5, and 10), and the results of studies of the temperature dynamics of the width of depolarized lines in Raman scattering of light (LRSL) (Refs, 4 and 16) clearly show that the widths of RLW and LRSL decrease upon approach to the critical stratification point. The results give grounds for assuming that upon approach to the critical point of the solution the character of the orientational motion of the molecules of the medium is changed.

The authors wish to thank A. S. Zolot'ko for help in conducting the experiments.

[1)] For sufficiently large frequencies, much higher than the reciprocal of the shortest relaxation time, the intensity of the RLW can depend on the frequency in accord with another law, in particular, exponentially. The authors did not investigate this frequency region in this work.

[2)] Equation (3) is cited by Wilson[14] without proof. We did not find in the literature a proof of the validity of replacing r by r_c in the well known formula for D_r.

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Adiabatic mechanism of broadening of zero-phonon lines in impurity-crystal spectra

O. N. Korotaev and M. Yu. Kaliteevskiĭ

Moscow State Pedagogical Institute

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It is demonstrated experimentally that the adiabatic mechanism of electron-phonon interaction is responsible for the temperature broadening of optical zero-phonon lines (ZPL) in the spectra of the impurity centers of crystals. A quantitative correlation is established between the rate of the temperature broadening of the ZPL and the nonspecularity of their accompanying phonon wings in the fluorescence and absorption spectra. It is shown that the quadratic electron-phonon interaction that leads to the broadening of the investigated ZPL is strong, i.e., it cannot be accounted for by perturbation theory. The temperature dependence of the Debye-Waller factor is investigated and it is established that the Herzberg-Teller interaction is reponsible for the formation of the phonon wing in the allowed electronic transition. The theory is compared with experiment without the use of free parameters.

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1. INTRODUCTION

It is known[1-3] that the homogeneous width of the optical zero-phonon lines (ZPL) in the spectra of impurity crystals exceeds by one or two orders, even at liquid-helium temperature, the natural width γ connected with the level lifetime τ by the usual relation $\gamma = \hbar/\tau$. Various mechanisms were proposed for the temperature broadening of the ZPL.[4-6] The most accepted was the adiabatic mechanism proposed by Silsbee.[6] He has