Z. Phys. B – Condensed Matter 73, 231–233 (1988)

Condensed Matter
Zeitschrift für Physik B

On the description of the temperature dependence of the transient grating signal in molecular crystals *

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Received January 7, 1988; revised version June 29, 1988

We present a description of temperature effects on the evolution of transient grating signals and report on the relationships among several seemingly different theoretical approaches to the description of transient gratings in molecular crystals.

1. Introduction

Transient grating [1–5] and Ronchi ruling [6, 7] experiments provide a powerful method for the investigation of the nature and extent of exciton motion in molecular crystals and similar systems. Until very recently, only two theoretically predicted signals [1, 8–13] have been available. They both show highly nonexponential behaviour for coherent exciton motion and exponential behaviour in the incoherent limit. While the incoherent limits are identical to each other, the coherent limits are quite different. The coherent signal calculated by Fayer [1] shows no oscillations, whereas, in Kenkre's theory [8–13] decaying oscillations are seen. In the former calculation a semiclassical approach is used and no explicit form of the initial density matrix is given, whereas, in the latter theory the initial density matrix is specifically taken to be random in the site representation. The oscillations which appear in the latter theory are a natural generalization of the oscillations that arise in a classical approach. Kenkre's theory [8–13] has been applied to experiment allowing mean free paths and diffusion constants to be extracted [4, 13, 14]. Recently, another theoretical signal has appeared in the literature [15, 16]. It involves an initial exciton population that occupies two Bloch states with wavevectors $\eta/2$ and $-\eta/2$, where η is the dimensionless wavevector of the grating given by $\eta=(4\pi a/\lambda)\sin(\theta/2)$, λ being the wavelength of the exciting light, θ the angle between the exciting laser beams and a the lattice spacing of the crystal. In the incoherent limit, this signal decays exponentially [16] as in the previous two theories, but in the coherent limit it is time-independent [15, 16] and therefore differs drastically from both. Furthermore, for intermediate coherence, it decays in a nonexponential fashion which does not show any oscillatory character.

Our task in the present paper is the inclusion of temperature effects in the description of transient gratings. This is an important undertaking because the grating experiments reported for singlets [3] were carried out at very low temperatures (up to 20 K and indeed as low as 1.8 K). Under these conditions, the inequality $k_B T > B$ where $B(\sim 50\ \mathrm{cm}^{-1})$ is the exciton bandwidth ($B=4$ V) in a one-dimensional system) does not apply. Of all the theoretical results on gratings discussed above, only one [1] contains temperature explicitly. However, as we shall show below, that result does not correspond to a true thermal distribution of probabilities and its physical significance is not entirely transparent. With the help of a formalism we constructed recently [17], we present here an initial density matrix which corresponds to an actual Boltzmann distribution of exciton *probabilities* and calculate the time dependence of the signal evolving from it.

2. Temperature effects and the relationship among different theoretical approaches

In [17] we introduced a general initial condition for the transient grating experiments which involves a

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* Work supported in part by the National Science Foundation under grant nos. DMR-850638 and DMR-8111434

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superposition of displaced pairs of wavevectors in the exciton Brillouin zone. Each of these pairs consists of wavevectors separated by the grating wavevector η but centered at arbitrary positions in the Brillouin zone. We showed that, starting from our general grating signal, we can obtain the two extreme cases discussed in the literature earlier: we arrive at the random initial density matrix signal [8–12] when a uniform distribution of the pair states is assumed over the zone, and at the single pair state result [15, 16] when only a symmetric pair is assumed. We shall now choose an appropriate intermediate superposition in order to get the temperature-dependent initial condition we seek. We note that the spatial distribution of the exciton density is decided purely by the off-diagonal elements of the density matrix in k-space. We can therefore use the freedom thus available in regard to the diagonal elements in k-space to construct an initial density matrix which corresponds to the known spatially sinusoidal distribution (characteristic of the grating wavelength η) but which also incorporates Boltzmann detailed balance among the k-space probabilities. Thus, we assume the following form for the initial density matrix

$$\rho^{kq}(t=0)=[\delta_{k,q}+\tfrac{1}{2}(\delta_{k,q+\eta}+\delta_{k,q-\eta})]\cdot[I_0(2V\beta)]^{-1}\,\mathrm{e}^{-2V\beta\cos k} \qquad (1)$$

where V is the (nearest neighbour) matrix element of the Hamiltonian describing exciton transport between sites, $\beta=1/k_B T$ is the inverse temperature and $I_0(x)$ is the modified Bessel function of zero order.

The diagonal elements $\rho^{kk}(t=0)$ do indeed possess the thermal distribution and a double Fourier transform shows immediately that the probabilities in site space, i.e. $\rho_{mm}(t=0)$, form a sinusoidal pattern with wavevector η. The transient grating signal $S(t)$ is proportional to the square of the amplitude of the inhomogeneity whose full form can be written conveniently as a convolution [17]

$$S(t)=\mathrm{e}^{-2\alpha t}\left[\int_0^t \mathrm{d}t'\,S_\alpha(t-t')\,S_c(t')\right]^2 \qquad (2)$$

where S_α describes the effect of scattering through the scattering rate α, and S_c is the signal in the coherent limit. In the light of (2) we need only discuss temperature effects on S_c. The coherent signal that results from (1) is

$$S_c(t)=[I_0(2V\beta)]^{-1}\,\mathrm{Re}\,J_0\left(b\left[(t-i\beta/2)^2-\left(\frac{\beta}{2}\cot(\eta/2)\right)^2\right]^{\frac{1}{2}}\right) \qquad (3)$$

where Re{ } denotes the real part, $J_0(x)$ is the Bessel function of first kind of zeroth order and $b=4V\sin(\eta/2)$.

As can be readily seen from (3), the coherent signal presented above reduces for high and low temperatures, to $J_0(bt)$ and unity respectively. These are the two coherent results for the signal when we start with the random initial condition and the pair state respectively.

It goes without saying that an actual thermalized density matrix, which depicts real thermal equilibrium and consequently zero off-diagonal elements in k-space, cannot correspond to any spatial inhomogeneity of the exciton probability. The physical picture underlying the choice of our initial condition (1) is that the excitons attain a Boltzmann distribution rapidly among their *probabilities* before the measurable destruction of the spatial inhomogeneity begins. Whether such a process does indeed occur or whether the appropriate description of the evolution of the grating does not involve any quasi-equilibrium is not the concern of the present discussion. The idea of the quasi-equilibrium [18] is similar in spirit to the situation in thermal conduction wherein "normal" processes, although unable to destroy the total phonon momentum, redistribute the phonons thermally with the given initial momentum. If the quasi-equilibration does occur, (1)–(3) that we have presented may be used for a possible description.

In attempting to include the effects of non-infinite temperature on the grating signals, we found [17] that, if the pair states are assumed initially to be in a certain pseudothermal distribution shown below, we obtain a signal which, in the coherent limit, reduces exactly to the expression obtained by Fayer [1] through semiclassical arguments. We comment here in passing that Fayer's result for the coherent signal S_c, given by

$$S_c(t)=[2\pi I_0(2\beta V)]^{-1}\cdot\int_{-\pi}^{+\pi}\mathrm{d}x\,\mathrm{e}^{-2\beta V\cos x}\cos(bt\sin x) \qquad (4)$$

can be written very simply as

$$S_c(t)=[I_0(2V\beta)]^{-1}J_0([(bt)^2-(2V\beta)^2]^{\frac{1}{2}}) \qquad (5)$$

The general pseudothermal signal [17] reduces to the results of [8–12] if the pseudotemperature is taken to be infinite and to those of [15, 16] if it is taken to be zero. We also see from (2) that Fayer's result [1] is identical to Kenkre's result [8–13] in the coherent limit, i.e. $J_0(bt)$, if $\beta=0$ (infinite temperature) and that these statements and (2) show explicitly the close relationships that exist among the signals given by the various authors. Fayer's signal corresponds, however, to an initial diagonal matrix whose diagonal elements in k-space are given by

$$\rho^{kk}(t=0)=\tfrac{1}{2}[I_0(2V\beta)]^{-1} \cdot [e^{-2V\beta\cos(k+\eta/2)}+e^{-2V\beta\cos(k-\eta/2)}] \qquad (6)$$

These diagonal elements, i.e., the probabilities in k-space, do not obey Boltzmann detailed balance. In other words, Fayer's initial state does not involve thermalized probabilities.

We can compare the two signals (3) and (5) after we perform the small angle approximation $\sin(\eta/2)\sim\eta/2$ in both of them. One gets, respectively,

$$S_c(t)=[I_0(2V\beta)]^{-1} \cdot I_0(2V\beta[1-(2\pi a/d)(t/\beta-i/2)^2]^{\frac{1}{2}}) \qquad (7)$$

$$S_c(t)=[I_0(2V\beta)]^{-1} \cdot I_0(2V\beta[1-(2\pi a/d)(t/\beta)^2]^{\frac{1}{2}}) \qquad (8)$$

where a is the lattice constant and $d=\lambda/2\sin(\theta/2)$ is the fringe length of the grating. The two formulas written above, although different in general, give for the parameters involved in the transient grating experiments as well as for the times relevant to the observable, very similar results.

3. Conclusion

Temperature enters into transient grating experiments in two ways: *(i)* one is related to the way the equation of motion drives the system towards the correct thermal equilibrium, and *(ii)* the other has to do with the intial conditions whenever one assumes a quasiequilibrium to occur initially. It is well known that in the former sense the Stochastic Liouville equation.

$$i\frac{\partial\rho_{mn}}{\partial t}=V(\rho_{m,n+1}+\rho_{m,n-1}-\rho_{m+1,n}-\rho_{m-1,n}) - i\alpha(1-\delta_{mn})\rho_{mn} \qquad (9)$$

which underlies our analysis, is not an appropriate equation of motion since it corresponds to an infinite temperature equilibration of the system. A completely satsfactory description of *(i)* is therefore out of bounds as long as we continue to employ the Stochastic Liouville equation (9) for the time evolution of the system. This problem may be addressed through the Kenkre-Brown prescription [19] which alleviates the related problem in calculations of the scattering function, since the scattering function is simply the Fourier transform of the transient grating signal calculated for an arbitrary wavevector k. However, important as it is, this problem is not under discussion in this paper. Instead, we have concentrated here on the question of how temperature may enter in the problem through the initial condition. Of the variety of initial density matrices that are compatible with the initial spatial inhomogeneity of the excitons, we have chosen (1) because it incorporates the correct Boltzmann weights in its probability distribution and may therefore be taken to describe a quasi-equilibrium. We have seen that it reduces to the appropriate limits and it gives the correct time behaviour when temperature is introduced into it. It is to be noted, however, that signals (7) and (8) are practically identical for the parameters and the time scale of the transient grating experiments reported so far.

We would like to thank Dr. Evita Vulgaris for valuable discussions.

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