

Fig. 3. Plot of  $\rho_e/\rho_T$  and of the reciprocal "magnetization" time vs. the absorption coefficient in GaAs.

at  $\ell_D \ll 1/\alpha$  and  $d \ll 1/\alpha$ . Linear extrapolation of  $f_1$  and  $f_2$  to the value  $\alpha = 0$  makes it possible to determine the values  $\tau$  and  $\tau_s$  corresponding to the volume ( $\tau_v$  and  $\tau_{sv}$ ). We obtained  $\tau_v = (2.5 \pm 0.3) \times 10^{-10}$  sec and  $\tau_{sv} = (9.6 \pm 1.2) \times 10^{-10}$  sec. The quantity  $\tau_s$  in the surface layer can be determined if there is additional information concerning the quantities  $d$  and  $\ell_D$ . For example, neglecting carrier diffusion, we can explain the experimental results as being due to the presence of a near-surface layer with thickness on the order of  $10^{-5}$  cm, in which  $\tau_s$  is smaller by one order of magnitude than  $\tau_{sv}$ .

It should be noted that an indication that the spin-relaxation time changes on going from the surface to the volume in semiconductors exposed to light is contained in a paper dealing with an EPR investigation [6].

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#### NEW DATA ON THE STRUCTURE OF OPTICAL ABSORPTION IN THE REGION OF ISOTOPIC-IMPURITY EXCITON STATES OF NAPHTHALENE CRYSTALS

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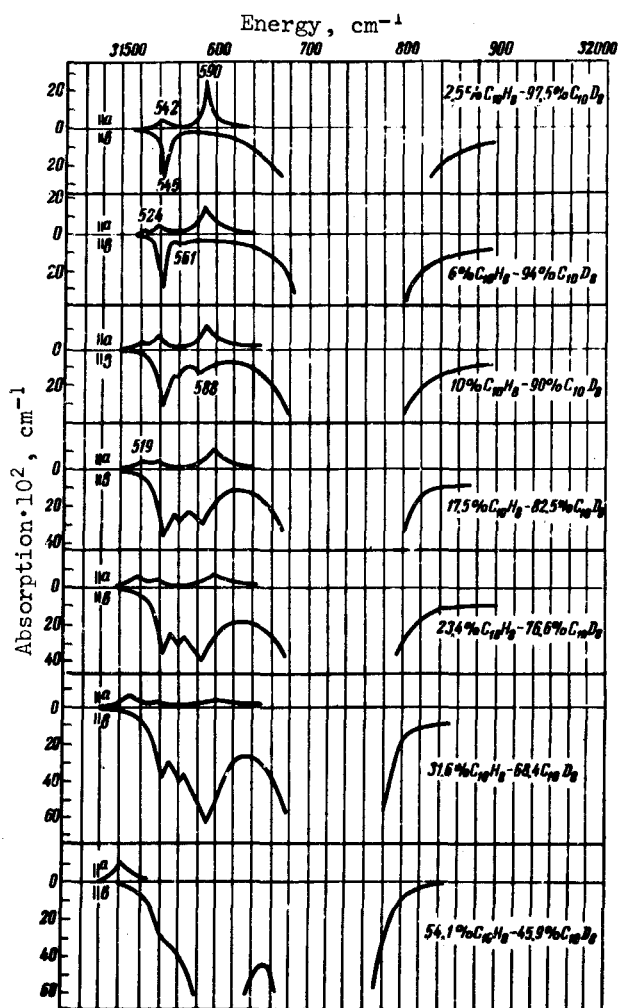
We have previously reported that the production of impurity excitons in mixed isotopic molecular crystals is accompanied by a smooth variation of the Davydov splittings in the electronic transition with increasing concentration of one of the mixture components. The corresponding conclusions were based on a qualitative analysis of the form of spectrum of optical absorption of such crystals as benzene [1] and naphthalene [2] at 20.4°K.

We have made detailed quantitative measurements of the low-temperature (4.2°K) exciton absorption in isotopically mixed naphthalene- $h_8$  ( $H_8$ ) and naphthalene- $d_8$  ( $D_8$ ) (DFS-13 spectrograph with linear dispersion 2 Å/mm). We used samples with thickness larger than 4  $\mu$ , in which neither cooling from the

melting temperature to room temperature nor further cooling to 4.2°K produced any mechanical internal stresses capable of distorting the spectral measurement results [3].

An analysis of the results shows that at appreciable impurity concentrations the spectrum reveals a distinct, never heretofore discussed fine structure. The figure shows the measured optical-absorption curves in the region of the lowest purely electronic transition for several crystal mixtures in the concentration interval up to 54% of  $H_8$ <sup>1)</sup>.

The following features of the absorption curves shown in the figure should be noted: 1) The absorption spectrum of the mixture is richer than the spectrum of the pure crystals, and the  $H_8$  admixture is represented not by a sharply polarized doublet, as would follow from the theoretical considerations [4, 5], but by at least six bands. 2) The positions of the bands in the observed fine structure are practically independent of the  $H_8$  concentration<sup>2)</sup>. When the latter increases one can note only the appearance and the disappearance of bands and the change of their absolute and relative intensities. 3) For a-polarization of the light incident on the crystal, it was established that the absolute intensity of the band due to a small  $H_8$  admixture, 31542  $cm^{-1}$ , decreases insignificantly with increasing concentration, although its relative strength decreases more sharply. The relative intensity of the 31524  $cm^{-1}$  band, which appears at ~6%  $H_8$ , first increases somewhat, and then decreases again. At approximately 10 - 18%  $H_8$  a band near 31519  $cm^{-1}$  appears in the spectrum, with an intensity that subsequently increases with the concentration. The intensity of the 31590  $cm^{-1}$  band (which corresponds to an extremely low  $H_8$  concentration to the A band of the Davydov doublet of the pure crystal  $D_8$ ) decreases continuously with increasing  $H_8$  concentration. 4) For b-polarization of the light incident on the crystal, three absorption bands were observed near 31545<sup>3)</sup>, 31561, and 31588  $cm^{-1}$ . The relative intensities of these bands, at low  $H_8$  concentrations, decrease with



<sup>1)</sup>The optical absorption in mixed crystals with small contents of  $D_8$  has on the whole an analogous structure.

<sup>2)</sup> Small shifts of the band maxima within the limits of several  $cm^{-1}$ , which were observed in the measurements of the spectra, will be discussed in a separate communication.

<sup>3)</sup>We attribute this band to a small admixture of  $H_8$  in the  $D_8$  crystal, and leave the question of the polarization splitting observed in this case open for the time being.

decreasing wavelength. With increasing  $H_8$  concentration, the relative intensities become redistributed and at a concentration of about 32%  $H_8$  the short-wave band becomes the strongest. 5) With increasing  $H_8$  concentration one observes a general broadening of the absorption bands, accompanied by a gradual smearing out of the fine structure. 6) The observed fine structure in the spectra of mixed crystals does not depend on their thickness, on the growth rate, or on the heat treatment of the single crystals. The structure was perfectly reproducible within the limits of errors ( $\sim 10\%$  in terms of intensity) in different samples having the same composition.

From the foregoing data it follows that on the whole the exciton splitting increases with increasing  $H_8$  concentration, if this splitting is determined by measuring the interval between the centers of gravity of the groups of bands for each polarization of the incident light. The general picture of the spectrum is in qualitative agreement with photographic data on the absorption spectra [2], but the previous interpretation was aimed only at separating the Davydov doublet for each chemical component.

The fine structure in the purely electronic spectrum of a mixed crystal can be interpreted by assuming that there exist in the sample single impurity molecules of  $H_8$ , located alongside pairs of more complicated aggregates made up of translationally-nonequivalent  $H_8$  molecules that are in resonant interaction. Because a number of investigations have demonstrated the short-range character of the interaction forces in the naphthalene crystal (see, e.g., [6]), we can confine ourselves in the estimate of the matrix elements of the pair interaction  $M_{ij}$ , with good accuracy, to only the nearest neighbors. Such neighbors are the translationally-nonequivalent pairs of molecules, and  $M_{ij} = M_{12}$ . If we assume that the Davydov splitting in the pure crystal is equal to  $8M_{12}$  ( $147 \text{ cm}^{-1}$ ), then we obtain for the resonant splitting in the pair a value  $2M_{12}$ , and for the larger formation this splitting can reach also  $4M_{12}$  (linear chain of translationally-nonequivalent molecules).

The most intense impurity band at sufficiently small  $H_8$  concentrations (2 - 3% and lower) corresponds, naturally, to single  $H_8$  molecules. Its position is  $31542 \text{ cm}^{-1}$ , which is an unsplit impurity term shifted away from the corresponding term in the pure crystal  $H_8$  as a result of the Rashba effect [7]. The doublet  $\sim 31525$  ( $\parallel \vec{a}$ ) -  $31562$  ( $\parallel \vec{b}$ )  $\text{cm}^{-1}$  for the resonant pair should then be observed and the doublet  $\sim 31508$  ( $\parallel \vec{a}$ ) -  $31582$  ( $\parallel \vec{b}$ )  $\text{cm}^{-1}$  for a sufficiently long chain of molecules; the respective splittings are 37 and  $74 \text{ cm}^{-1}$  <sup>4</sup>).

A comparison of these estimates for the positions of the doublets with the observed structure is, in our opinion, convincing evidence that the bands  $31524$  ( $\parallel \vec{a}$ )  $\text{cm}^{-1}$  and  $31561$  ( $\parallel \vec{b}$ )  $\text{cm}^{-1}$  correspond to a resonant pair, and a considerable contribution to the bands  $31519$  ( $\parallel \vec{a}$ )  $\text{cm}^{-1}$  and  $31588$  ( $\parallel \vec{b}$ )  $\text{cm}^{-1}$  is made by the branched molecule chains. The obtained band frequencies for the resonant pair are in good agreement with the results of Hanson [8], who observed a band  $31527 \text{ cm}^{-1}$  ( $\parallel \vec{a}$ ) in the spectrum of a very small impurity ( $\sim 1.4\%$   $H_8$ ) and who proposed the same interpretation for it.

As expected, an increase of the  $H_8$  concentration is first accompanied by an increase in the number of resonant pairs, and then by a decrease of their relative concentration and an increase of the number of larger aggregates. Nor is it surprising that the spectrum contains no individual maxima corresponding to resonant groups of four or groups of five impurity molecules, since the probability of their formation becomes noticeable already at such total impurity

<sup>4</sup>) Naturally, the foregoing estimates of the band positions are not very accurate because of the possible small displacements of the impurity bands as the result of quiresonant interactions.

concentrations ( $\sim 50\%$   $H_2$ ) at which it is practically impossible for them to be isolated.

It should also be noted that when impurity exciton states are analyzed by the coherent-potential method [5, 9, 10], the possibility of formation of discrete aggregates such as groups of two, groups of three, etc. is excluded, and a statistical averaging of the configuration is proposed. Therefore, the absorption curves obtained in this manner for the exciton states can apparently be set in correspondence only with the envelope of the experimental spectrum.

Finally, the independence of the fine structure and of its quantitative characteristics of the heat treatment of the samples is evidence that there is no macroscopic lamination in the mixed  $H_2$ - $D_2$  crystals, which has in general a rather low probability in such isotopic systems.

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#### OBSERVATION OF MAGNON-PHONON INTERACTION IN ANTIFERROMAGNETIC $MnCO_3$

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Parametric excitation of spin waves was recently observed experimentally in the antiferromagnetic crystals  $CsMnF_3$  [1 - 3] and  $CuCl_2 \cdot 2H_2O$  [4]. It is important that the nonlinear interaction responsible for the parametric excitation of the spin waves in an antiferromagnet couples the oscillations of the variables belonging to different branches of the spin-wave spectrum, and, in contrast to ferrites, is of exchange origin [5].

We have observed parametric excitation of spin waves in antiferromagnetic  $MnCO_3$ , and thereby observed resonant interaction of excited spin waves with phonons.

The excitation of the spin waves was revealed also, just as in [3], by the additional microwave-power absorption occurring in the sample<sup>1)</sup> placed in a high-Q resonator in such a way that the static and high-frequency fields were parallel to each other and lay in the basal plane of the crystal. The detected

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<sup>1)</sup>We used  $MnCO_3$  single crystals grown by the hydrothermal method by N.Yu. Ikornikova and V.R. Gakel' of the Crystallography Institute.