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NONRADIATIVE RELAXATION AND THE JAHN-TELLER EFFECT OF Fe^{2+} IN III-V SEMICONDUCTORS

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The quantum yield of the Fe^{2+}($^5T_2$-^5E) luminescence in InP, GaP, and GaAs is determined by means of calorimetric absorption and calorimetric transmission spectroscopy at mK temperatures. The radiative transition rate is found to be independent of the host material and explained by configuration mixing. The nonradiative relaxation rate reflects the electron-phonon coupling strength in the host materials. A correlation between the multiphonon emission probability and the isotope splitting is observed, indicating the coupling of local T_2 modes to the excited $^5T_2$ state to be crucial.

Introduction

The optical properties of Fe centers in III-V materials have been extensively investigated for many years resulting in a well established energy scheme.[1-5] Most prominent is the intracenter ^5E-$^5T_2$ transition of Fe^{2+} on cation sites leading to sharp structures in absorption and emission. The fine structure of the ^5E ground state is well established and its interpretation needs a weak Jahn-Teller effect involving E-type modes.[6] Only insufficient data exist for the $^5T_2$ excited state hampering a reliable determination of the electron-phonon coupling. Recently, a coupling to T_2-type modes has been deduced[7] from observed isotope splittings in the order of some 10 μeV/nucleon.[3,4,5]
The decay times of the $^5T_2$-^5E luminescence were found in the 10 μs range at liquid He temperatures.[8-10] However, the nonradiative relaxation processes involved in the $^5T_2$-^5E transition are not well understood, yet. In the present paper we report on calorimetric absorption results, which enable us to determine the low temperature quantum yield of the $^5T_2$-^5E luminescence. The radiative and nonradiative relaxation rates are discussed, pointing out the close relationship between the dynamical and structural properties of the Fe center. In particular, a correlation between the nonradiative relaxation rate and the isotope shift is stated, demonstrating the crucial importance of a dynamical Jahn-Teller effect involving local T_2 modes in the excited $^5T_2$ multiplet for both effects.

Experimental Results

Calorimetric absorption spectroscopy (CAS) at mK temperatures is a powerful tool to investigate nonradiative relaxation processes in semiconductors.[11] It detects the sample heating upon optical excitation in dependence on the photon energy and, thus, represents a phonon emission excitation spectroscopy. All phonons generated contribute to the signal and, thus, only the excitation spectrum yields information about their origin. The absorbed light power P_{abs} (obtained from calorimetrically detected transmission spectra taking into account reflection at the sample surfaces) and the generated heat power P_{CAS} are determined quantitatively yielding the nonradiative relaxation part $Q=P_{CAS}/P_{abs}$.[11]
Fig.1 gives experimental results for the ^5E-$^5T_2$ absorption of Fe^{2+} in InP, GaP, and GaAs.

The spectra resemble typical low temperature absorption spectra.[1-5] At 45 mK only the Γ_1 ground state of the ^5E multiplet is populated and, thus, only transitions into Γ_5 states are dipole allowed. Consequently, the dominating low energy line A and the broader transition B are attributed to transitions ending in the Γ_5 ground and the first excited Γ_5' state of the $^5T_2$ multiplet, respectively. The sharp resonance GM in InP and GaP is attributed to a local mode replica of the transition line A.

Comparing the P_{CAS} and the P_{abs} signals it is obvious that the relaxation of the excited $^5T_2$ level generates a considerable number of phonons. A detailed analysis of the A transition yields nonradiative recombination parts Q of (53±5)%, (74±4)%, and (65±5)% in InP, GaP, and GaAs, respectively. For the B and the GM transition we obtain slightly higher values of (58±5)% and (77±4)% in InP and GaP, respectively. These deviations are significant in spite of the absolute experimental error. The nonradiative relaxation of the Γ_5' into the Γ_5 state and the generation of the local phonon GM explain the increased heat generation, respectively.

The quantum yield η of a transition is defined via the transition rates and, thus, in general not obtained directly from the CAS result Q.[12,13] However, the $^5T_2$-^5E transition can be treated as a two level system if phonons generated in nonradiative intralevel relaxation processes and phonon-assisted radiative processes are taken into account. Exciting the A transition intralevel relaxation is avoided and the phonon sideband of the $^5T_2$-^5E luminescence is weak, which means that phonon assisted radiative processes can be neglected in view of the overall experimental error. Thus, the quantum yield η of the Fe^{2+}($^5T_2$-^5E) transition is directly given by 1-Q(A). The radiative (W_r) and nonradiative (W_{nr}) decay rates of the $^5T_2$ state are given by the luminescence decay time τ and the quantum efficiency η:

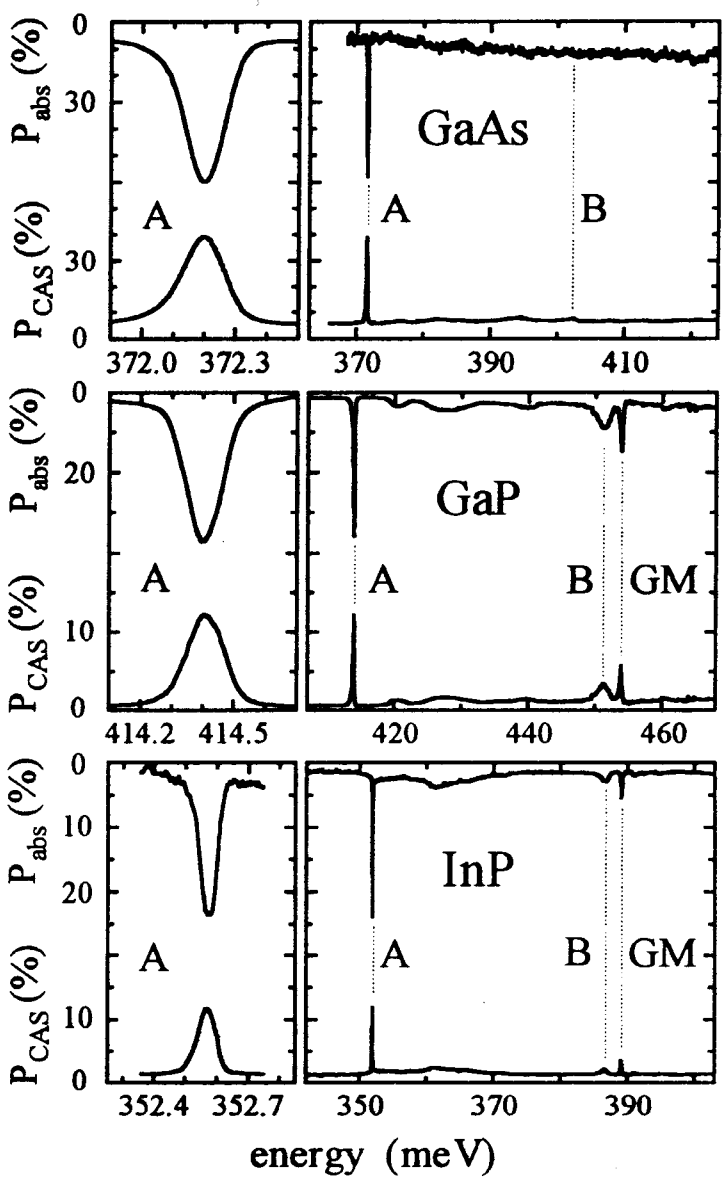

Fig.1: Calorimetric absorption spectra in comparison to the absorbed light power of the Fe^{2+}(^5E-$^5T_2$) transition in InP, GaP, and GaAs. The powers are given with respect to the incident light power.

$$W_r = \frac{\eta}{\tau} \quad \text{and} \quad W_{nr} = \frac{1-\eta}{\tau}. \qquad (1)$$

Tab.I summarizes the experimental results and gives the calculated radiative and nonradiative transition rates.

Tab.I: Quantum yield (η), luminescence lifetime (τ), and the resulting radiative (W_r) as well as nonradiative (W_{nr}) transition rate of the Fe^{2+}($^5T_2$-^5E) transition in III-V semiconductors and ZnS.

	η (%)	τ (μs)	W_r (kHz)	W_{nr} (kHz)
InP	47	11[8]	43	57
GaP	26	6.6[14]	39	114
GaAs	35	8.5[10]	41	77
ZnS[15]	10	5.5	18	165

Discussion

Tab.I demonstrates that at low temperatures the radiative and nonradiative processes are equally important for the Fe^{2+}($^5T_2$-^5E) transition. Quantum efficiencies below 50% are observed. The variation of the lifetime and the quantum efficiency is caused by the nonradiative processes.

The radiative transition rates W_r are found to be equal within the margins of error. The mean value of $4 \cdot 10^4$ Hz corresponds well to the dipole transition rate of $6.7 \cdot 10^4$ Hz deduced from absorption results for InP:Fe.[8] The oscillator strength of d-d transitions results from the admixture of p-like wavefunctions by covalent bonding as well as configuration mixing (enabled by the lack of inversion symmetry).[12] For transitions between near midgap levels, as the Fe^{2+}($^5T_2$-^5E) transition, configuration mixing dominates, which is almost independent of the host material. This interpretation is supported by the similar radiative transition rate of $1.8 \cdot 10^4$ Hz found for ZnS:Fe^{2+},[15] tab.I.

We attribute the nonradiative relaxation of the $^5T_2$ state to a multiphonon emission process. Auger as well as carrier trapping processes can be excluded for semi-insulating samples and infrared excitation densities in the μWcm^{-2} region. In the weak coupling limit the nonradiative transition probability depends exponentially on the number of phonons needed to span the transition energy.[16] For Fe^{2+} no such trend is observed and, additionally, the nonradiative transition rates are too high for the weak coupling limit. Thus, the stronger electron-phonon interaction of 3d centers explains the enhanced multiphonon transition probability.[12] However, the Fe^{2+}(^5E-$^5T_2$) absorption and emission bands exhibit only weak sidebands excluding a strong electron-phonon interaction. Calculations show only a weak coupling of E-type modes to the ^5E ground state, but indicate a moderate coupling for the $^5T_2$ excited state,[6] which, thus, should account for the determined nonradiative transition rates.

The Jahn-Teller coupling in the $^5T_2$ state can be evaluated on the basis of observed isotope shifts.[7] In semiconductors the mass dependence of impurity states is a consequence of mass sensitive local phonons (T_2 modes) contributing to the total energy. Isotope shifts of optical transitions are a difference effect and in the case of intracenter 3d transitions a consequence of the vibronic character of the involved states.[17,18] For Fe^{2+} the Jahn-Teller coupling in the ^5E ground state can be neglected, giving

$$\frac{dE_{opt}}{dM} = \frac{dE_{exc.}}{dM} - \frac{dE_{gr.}}{dM} = \left(\frac{dE_{^5T_2}}{d\hbar\omega_{T_2}} - \frac{3}{2} \right) \cdot \frac{d\hbar\omega_{T_2}}{dM} > 0. \qquad (2)$$

(A detailed discussion of eq. (2) is given in refs. 17 and 18.) Eq. (2) predicts a *positive* isotope shift as observed and makes its *magnitude* a measure for the coupling of the $^5T_2$ excited state to T_2-type modes. Comparing the nonradiative transition rate W_{nr} with the respective isotope shift, fig.2, a distinct correlation can be stated. This demonstrates the close correlation between the Jahn-Teller effect in the excited $^5T_2$ state and the multiphonon relaxation process. Additionally, the higher nonradiative transition rate observed for ZnS,[15] tab.I, corresponds well to the stronger electron-phonon coupling in the II-VI compounds.[6] A weak dynamical Jahn-Teller effect is found to enhance the nonradiative transition rate by orders of magnitude.

The presented results make the Fe^{2+} center an interesting model system for calculations of the electron-phonon interaction, which determines not only the fine structure but also the relaxation mechanisms.

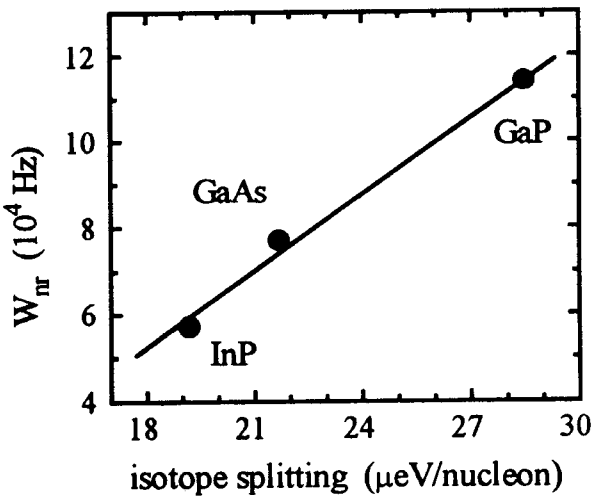

Fig.2: *The nonradiative relaxation rate W_{nr} of the Fe^{2+}($^5T_2$-^5E) transition versus the respective isotope splitting. The isotope shift is a measure for the coupling of the excited $^5T_2$ state to local T_2 modes.*

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