HOT LINES AT mK TEMPERATURES: $^3He/^4He$ CALORIMETRIC ABSORPTION SPECTRA OF THE $Fe^{3+} \rightarrow Fe^{2+}$ CHARGE TRANSFER TRANSITIONS IN GaP

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Temperature dependent calorimetric absorption experiments in the mK temperature range are demonstrated to resolve ground state splittings of the order of μeV of optical transitions usually accessible only to microwave experiments. The $Fe^{3+}(^6A_1)$ ground state of the Fe^{3+}/Fe^{2+} charge transfer transition in GaP, split into Γ_7 and Γ_8 sublevels, is investigated as a model system. The size of this extremely small splitting of about 15μeV is derived from a detailed investigation of the temperature dependence in the range 45mK to 500 mK of a recently discovered quintet (a'-e') of narrow bound state absorption lines at 825 meV and a doublet (a, b) at 835 meV. While the relative intensity of the lines is found not to vary at all between 10 K and 0.5 K it starts to change considerably at lower temperatures. Thermalization between the substates of the Fe^{3+} level is identified to cause the temperature dependence. A detailed numerical analysis of the results not only yields the degeneracy ratio of the doublet, but also the various oscillator strength ratios to the excited states of the transition. In addition, our results prove unambiguously that all seven absorption lines arise from the Fe^{3+} ground state, which was partly disputed until now.

1. Introduction

Transition metal ions in semiconductors are of great interest because their incorporation is often precondition for semiinsulating behaviour of the material. They are known to be of importance in controlling carrier lifetimes /1/ and the energy position of the Fermi level. Moreover, they were found to form bound electron-hole states near the band edge /2/.

Recently, the electronic structure of Fe in various III-V compounds found particular attention /3-9/ and was studied in great detail. Juhl et al /3/ have shown that the $Fe^{3+} + \hbar\omega \rightarrow Fe^{2+}$ (^5E or $^5T_2$) + e^+ photoionizing absorption bands are preceded by a series of extremely narrow lines caused by transitions to bound states. This observation was based on the development of a novel, highly sensitive technique for performing absorption experiments, called calorimetric absorption spectroscopy (CAS) /10/. The multiplicity and the fine structure of these novel narrow absorption lines reflect the details of the energetic structure of the two different Fe^{2+} states (^5E and $^5T_2$). However, no information on the Fe^{3+} ($^6A_1$) ground state of these transitions could yet be derived from such experiments.

It is the purpose of this paper to present for the first time information on a doublet splitting of a few μeV of the $^6A_1$ ground state, on the multiplicity of the two levels, and on the relative oscillator strength from absorption spectroscopy. The measurements are performed by means of CAS at mK temperatures /11/ where extreme sensitivity for the detection of particularly small absorption is reached. Our experiments demonstrate for the first time that a pronounced temperature dependence of optical absorption spectra can be observed at such low temperatures if small ground state splittings exist.

2. Experimental

The experimental setup for CAS at mK temperatures is described in Ref. /11/. The method is based on the increase of sample temperature caused by the emission of phonons during the nonradiative recombination to thermal equilibrium of the excited state. The sample is monochromatically illuminated, and a CAS spectrum is detected by measuring the change of the sample temperature in dependence on excitation wavelength.

A typical CAS spectrum of Fe doped GaP at 0.5 K as known from Ref. /4/ is shown in Fig. 1 (uppermost spectrum). The spectrum was observed to be temperature independent in the range 0.5 K to 10 K. A series of narrow lines is observed located below the onset of the $Fe^{3+} + h\omega \rightarrow Fe^{2+}(^5E) + e^+$ charge transfer transition in GaP. A fine structure consisting of five peaks labeled a'...e' occurs at photon energies of 0.8242 eV and above. In addition, two lines a and b can be seen around 0.833 eV and 0.8344 eV. Corresponding transitions have already been observed by us and other authors /3, 5-9/ at the onset of the $Fe^{3+} \rightarrow Fe^{2+}(^5E)$ photoionizing absorption bands in InP and GaAs.

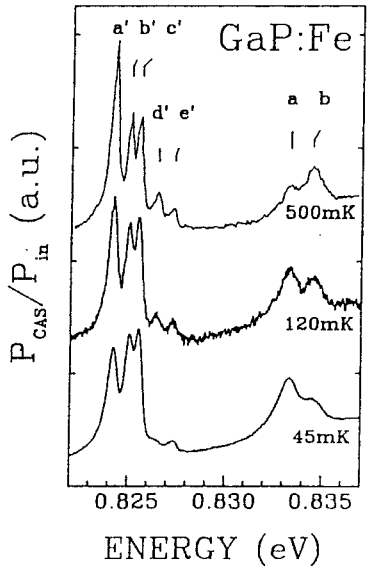

Fig. 1
Calorimetric absorption spectra of the narrow lines a'...e', a, b at different temperatures.

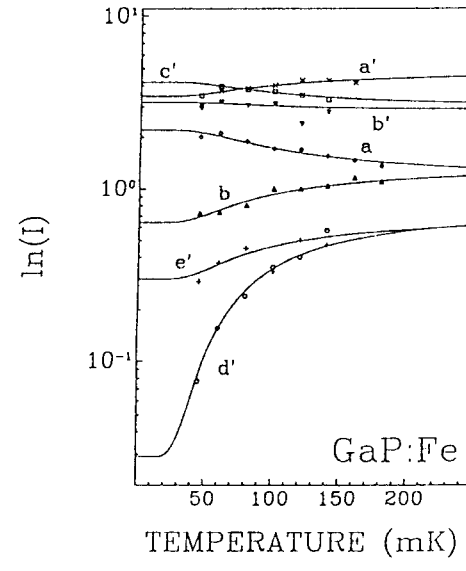

Fig. 2
Temperature dependence of the lines a' ...e', a, b. The curves represent a theoretical fit for a ground state splitting of 14.5 μeV.

Fig. 1 shows that the relative intensities of the lines start to depend strongly on temperature below 500 mK. At 45 mK the c' line dominates and the d' line nearly disappears. In addition, the intensity ratio between the a and b lines at 45 mK is reversed with respect to the 500 mK spectrum. This temperature dependence directly reflects the thermal population changes of an unresolved splitting of the ground state. We note that the individual linewidths of nearly 1 meV are much broader than the ground state splitting.

A quantitative analysis of the temperature behaviour is represented in Fig. 2. Here, the intensities of the seven lines a'...e', a, b are plotted as a function of temperature. The CAS spectra are calibrated at each temperature. The integrated intensities are evaluated from a fit of the spectral lineshape. Assuming a doublet splitting ΔE of the ground state the temperature dependence I_i of the different lines is given by:

$$I_i(T) = \frac{A f_{1i}}{1 + \frac{g_2}{g_1} e^{-\Delta E/kT}} \left\{ 1 + \frac{f_{2i}}{f_{1i}} \frac{g_2}{g_1} e^{-\Delta E/kT} \right\}$$

f_{2i}, f_{1i} are the oscillator strengths for transitions between the two ground states 1, 2 and the excited states i. A is a constant and g_2/g_1 is the ratio of the degeneracies. The fit parameters obtained are summarized in Tab. 1. Although the intensities of the seven lines vary very differently with increasing temperature, an accurate fit is obtained with the same activation energy of (15±3) μeV for all lines (see Tab. 1). This value is in good agreement with the known fine structure splitting of the $^6A_1(S)$ ground state of Fe^{3+} in GaP of 14.5 μeV /12/, determined by ESR spectroscopy.

	a`	b`	c`	d`	e`	a	b
ΔE [μeV]	14.5	14.5	14.5	14.5	14.5	14.5	14.5
g_2 / g_1	2	2	2	2	2	2	2
f_{2i} / f_{1i}	1.6	0.8	0.5	> 40	3	0.2	2.7
$A\ f_{1i}$	3.5	3.2	4.2	< 0.03	0.3	2.2	0.6

Tab. 1:
Fit parameters of the theoretical curves in Fig. 2.

3. Discussion

Our experiments show for the first time unambiguously that all seven lines a'...e' and a, b are originating from the same ground state. Furthermore, it becomes evident that all lines are caused by unperturbed Fe. The ratio of degeneracy g_2/g_1 is compatible with the splitting of the ground state into a Γ_8 and a Γ_7 level /12/. The Γ_8 level is energetically above the Γ_7 level. Additionally, due to their different temperature behaviour it becomes clear that the lines a and b are not phonon replicas of the lines a' and b'.

Detailed information about the final bound electon-hole states is obtained from the energy spacing between the different lines. The energy spacing between the lines a and b is very close to the splitting of the ^5E level of Fe^{2+} known from intracentre luminescence experiments /13/ which suggests an interpretation in terms of a (Fe^{2+},e^+) complex /5/. The splitting of the dominating quintet a'-e', however, is smaller. Based on similar observations for InP:Fe excitons bound to isoelectronic Fe^{3+} have been proposed to cause these lines /3, 4/. A consistent interpretation of all lines, on the other hand, is obtained by taking into account an exchange interaction between the Fe^{2+} centre and the hole in the (Fe^{2+},e^+) complex which scales with the localization of the hole. Here, the a'-e' lines are assigned to strongly localized $(Fe^{2+}, e^+_{n=1})$ and the a,b lines to $(Fe^{2+},e^+_{n=2})$ states with a weaker localized hole. The corresponding level scheme describing all spectra of Fig. 1 is shown in Fig. 3.

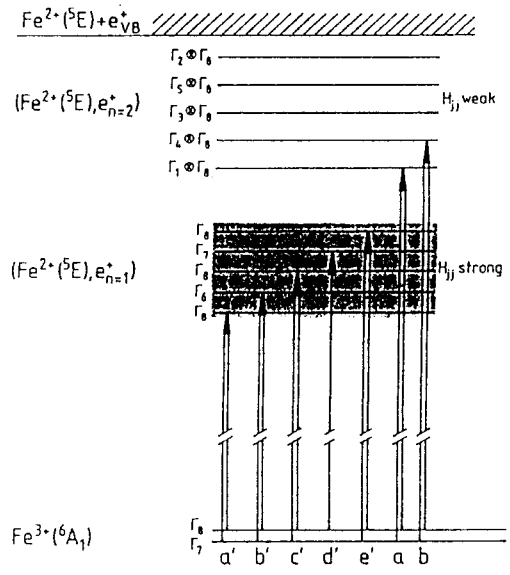

Fig. 3:
Term scheme of the $Fe^{3+} \rightarrow (Fe^{2+}(^5E),e^+)$ transitions

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