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1991 J. Phys.: Condens. Matter 3 5099

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Magneto-optical rotatory dispersion of some non-linear crystals

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Received 8 November 1990, in final form 26 February 1991

Abstract. We measured the magneto-optical rotatory dispersion (MORD) of eight non-linear KDP-type crystals: RDA, KDA, CDA, ADA, DRDA, DCDA, KDP and RDP. From our data we proceed to calculate the magneto-optic anomaly γ -factor for each crystal. We also calculate the energy gap by fitting our data to the BHL and KLN formulae, respectively. Finally, we make a comparison between the values of E_g obtained by the MORD method with those calculated from optical dispersion data. The effect on the γ -values and on E_g due to the substitution of cations and/or anions, as well as the deuteration of the samples, is discussed.

1. Introduction

Magneto-optical rotatory dispersion (MORD) of semiconductors and insulators is an important tool for studying the properties of materials, such as band gaps, as well as for obtaining insight into the nature of the corresponding optical transitions: direct or indirect. Among all the materials, we are particularly interested in studying the KDP isomorphous crystals because they combine excellent non-linear optical properties with fairly good magneto-optical rotation capabilities. In this work we carried out measurements of the Verdet constants of several KDP isomorphous crystals as a function of the wavelength in the visible region of the spectrum. In all, we investigated eight different crystals, two of them being deuterated with a very high degree of deuteration. The crystals that we studied were four dihydrogen arsenates (rubidium dihydrogen arsenate (RDA), potassium dihydrogen arsenate (KDA), caesium dihydrogen arsenate (CDA) and ammonium dihydrogen arsenate (ADA)), two dihydrogen phosphates (potassium dihydrogen phosphate (KDP) and rubidium dihydrogen phosphate (RDP)), as well as two deuterated dihydrogen arsenates (deuterated rubidium dihydrogen arsenate (DRDA) and deuterated caesium dihydrogen arsenate (DCDA)). The magneto-optical properties of three of these crystals have already been studied in [1, 2]: KDP, KDA and ADA. They were also included in our study for completeness.

After measuring the Verdet constant dispersion of all these crystals, we shall proceed to calculate some physical significant parameters such as the magneto-optical γ -factor of the crystals and their energy gap E_g . The energy gap will be found by fitting our data to the Boswarva–Howard–Lidiard (BHL) and Kolodziejczak–Lax–Nishina (KLN) formulae. We shall also calculate the parameter values for a fitting curve of our Faraday rotation dispersion data, one for each sample, which is good for interpolation purposes in the visible region of the spectrum. Finally, on the basis of our results we shall discuss

the effect on the properties of the crystals due to the substitution of anions and/or cations as well as the influence of the deuteration of the KDP isomorphs.

2. Experimental procedure

The Faraday rotatory dispersion of our samples was measured using a high pulsed magnetic field, with a pulse width of about 1.5 ms at its base. That magnetic field pulse was generated by the discharge of a bank of capacitors of 500 μF on an air core solenoid, at a maximum charging voltage of 5 kV. The total length of the magnet was 32 mm with an inner diameter of 25 mm. 140 turns of copper wire were wound in an eight-layer configuration, giving a total inductance of 384 μH . The solenoid was forced-air cooled in order to keep the sample at room temperature. At the maximum power supply voltage it is possible to reach a magnetic field with a peak value of over 130 kG.

The magnetic rotation of our samples was measured using the null method, which has been described in some of our previously published papers [3, 4]. In order to calibrate our magnet we used a rod of HOYA FR-5 glass, with a length of 10 mm. We chose our glass sample to be of the same length as the samples studied, in this way avoiding the necessity for any additional correction due to the axial magnetic field non-homogeneities. The value of the Verdet constant of this glass at the He-Ne laser wavelength was estimated to be $V = 0.245 \text{ min G}^{-1} \text{ cm}^{-1}$, which corresponds to the average value of the data given in [5, 6]. We measured the Verdet constant of our samples for seven different wavelengths, corresponding to the laser lines from a He-Ne laser and an argon laser, covering from the red region up to the blue-violet region of the spectrum.

3. Experimental results

We have a total of eight crystal samples to be studied by the MORD method. They are the phosphates KDP (KH_2PO_4) and RDP (RbH_2PO_4), the arsenates KDA (KH_2AsO_4), ADA ($\text{NH}_4\text{H}_2\text{AsO}_4$), CDA (CsH_2AsO_4) and RDA (RbH_2AsO_4), and two deuterated crystals DRDA and DCDA, both with a very high degree of deuteration. All our samples were supplied by Quantum Technology Inc. (Orlando, FL, USA) with a 10 mm length and were cut at 0° with respect to the tetragonal c axis. We proceeded to orient the samples with their optical axis parallel to the magnetic field by using the Maltese-cross method. This alignment was quite important because of the birefringence of our samples, which can introduce significant errors in the optical rotation measurements, leading to incorrect values for the Verdet constant. The seven laser lines that we used to study the samples were 0.6328 μm of the He-Ne laser and the six argon lines: 0.5145, 0.5017, 0.4965, 0.4880, 0.4765 and 0.4579 μm . All our measurements were carried out at approximately the same magnetic field peak intensity: between 60 and 80 kG. The temperature of the samples was monitored with a thermocouple.

For diamagnetic materials such as the crystals under study in this work, the Verdet constant can be related to the optical dispersion through the well known Becquerel relation

$$V = (e/2mc^2)\gamma\lambda(dn/d\lambda) = 1.01\gamma\lambda(dn/d\lambda) \quad (1)$$

where V ($\text{min G}^{-1} \text{ cm}^{-1}$) is the Verdet constant, λ (μm) is the wavelength $dn/d\lambda$ (μm^{-1}) is the optical dispersion of the material and γ is the magneto-optical

Table 1. Verdet constants at a wavelength of $0.6328 \mu\text{m}$ and the average γ -factor for the eight KDP-type crystals.

Crystal	This work		Koralewski's work	
	V ($\text{min G}^{-1} \text{cm}^{-1}$)	γ -factor	V ($\text{min G}^{-1} \text{cm}^{-1}$)	γ -factor
RDA	0.0212	0.705	—	—
KDA	0.0222	0.705	0.0238	0.856
CDA	0.0223	0.72	—	—
ADA	0.0227	0.68	0.0244	0.624
DRDA	0.0214	0.75	—	—
DCDA	0.0220	0.795	—	—
KDP	0.0128	0.59	0.0124	0.513
RDP	0.0128	0.61	—	—

anomaly factor. The constant $e/2mc^2 = 1.01 \text{ min G}^{-1} \text{cm}^{-1}$ is obtained using the following values for the electron charge, the electron mass and the speed of light: $e = 4.8 \times 10^{-10} \text{ esu}$, $m = 9.1 \times 10^{-28} \text{ g}$ and $c = 3 \times 10^{10} \text{ cm s}^{-1}$, respectively.

The magneto-optical anomaly factor, which is not constant throughout the optical spectrum, increases slightly from the red to the violet for almost all known materials. Higher values for γ , close to unity, indicate that the bonds in the material are of ionic type, whereas a low value for γ shows covalent-type bonds [7, 8]. In table 1 we summarize the values of the Verdet constant for all the crystals at a wavelength of $0.6328 \mu\text{m}$, including also the value of the γ -factor averaged over the whole range of wavelengths that we studied. The optical dispersion $dn/d\lambda$ was calculated for each sample by using the refractive index data published by Kirby and DeShazer [9]. For comparison we also show in the same table, the values reported by Koralewski [1] for the Verdet constant at $0.6328 \mu\text{m}$ and the γ -factor of the three crystals KDP, KDA and ADA.

We fitted our data to the following inverse power series expansion:

$$V(\lambda) = A + B\lambda^{-2} + C\lambda^{-4} \quad (2)$$

where V ($\text{min G}^{-1} \text{cm}^{-1}$) is the Verdet constant, λ (μm) is the wavelength, and A , B and C are a set of constants, different for each sample. Although the A , B and C constants cannot be directly correlated to any physical parameter, this fitting equation is still very useful when it is desired to make a quick calculation of the Verdet constant for some intermediate wavelength. A maximum deviation of 3% was found between interpolation curves and our corresponding experimental data for only three of the eight crystals that we studied (ADA, RDA and DCDA) which showed slight surface damage because of their higher hygroscopic character. For the other samples the fitting was better than 1%. In table 2 are displayed the values of A , B and C for each crystal.

Typical dispersion curves for the Verdet constant are shown in figures 1 and 2. In figure 1 we can observe the striking effect of the substitution of the anion group PO_4^{3-} by AsO_4^{3-} , whereas in figure 2 is shown the effect of deuteration of the samples. It can be seen from our data that the Verdet constants of the arsenates are on average 70% higher than those of the phosphates. On the other hand, the effect of changing only the cation is smaller, being in some cases the difference of the order of the experimental error; so, it is not possible to get any clear correlation between the value of the Verdet constant and the cation position in the periodic table or the cation structure as in

Table 2. Coefficients for the interpolation equation $V = A + B\lambda^{-2} + C\lambda^{-4}$, with V in minutes per gauss per centimetre and λ in micrometres.

Crystal	$A (\times 10^{-2})$	$B (\times 10^{-3})$	$C (\times 10^{-4})$
RDA	-0.777	1.246	-3.416
KDA	-0.077	0.864	2.272
CDA	-0.200	0.923	2.033
ADA	-0.132	0.925	1.516
DRDA	-0.113	0.836	2.646
DCDA	-1.841	1.862	-9.640
KDP	-0.141	0.570	-0.005
RDP	-0.126	0.541	0.825

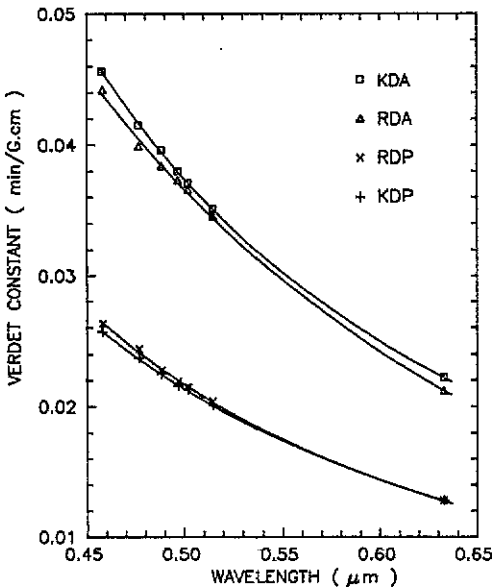


Figure 1. Verdet constants of KDA, RDA, RDP and KDP as a function of the wavelength: —, interpolation curve given by equation (2) with the values of A , B and C taken from table 2. The values of V for arsenates are around 70% higher than for phosphates.

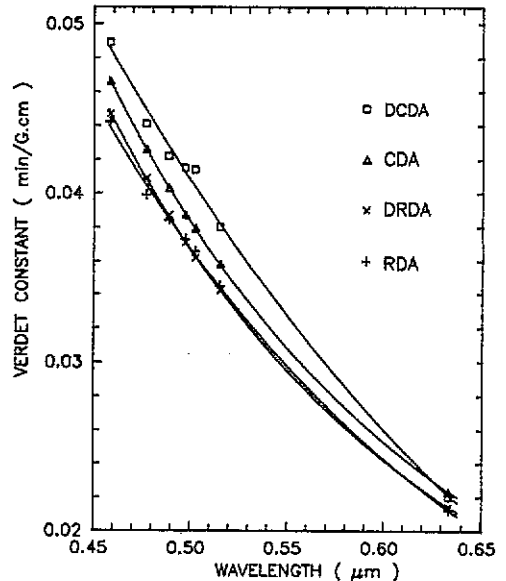


Figure 2. Verdet constants of DCDA, CDA, DRDA and RDA as a function of the wavelength, showing the effect of the deuteration of the samples: —, interpolation curve given by equation (2) with the values of A , B and C taken from table 2.

NH_4^+ . Deuteration of the samples causes an increase in the value of V ; this effect is strong in the case of CDA and quite small for RDA. Nevertheless, because we studied only two deuterated samples, we could not draw any further conclusions concerning the effect of deuteration.

The degree to which the bonds in our crystals are ionic or covalent is given by the observed values for the average magneto-optic anomaly factor $\bar{\gamma}$. The existence of three different and well defined groups is observed: the first group, formed by KDP and RDP, shows the lowest value for $\bar{\gamma} \approx 0.60$, in the second group we have ADA, CDA, RDA and CDA with $\bar{\gamma} \approx 0.70$ and finally the third group consisting of DRDA and DCDA has a value

of $\bar{\gamma} \approx 0.77$. So, we can conclude from our data that the substitution of the anion group PO_4^{3-} by AsO_4^{3-} and the posterior deuteration steadily increases the ionic character of the crystal bonds.

An attempt was made to correlate the value of the Verdet constant of the crystals with their corresponding Curie temperature T_C , as a check on Koralewski's [1] proposal, but that correlation was not confirmed at all. Perhaps the dependence of V on T_C is only restricted for the case when there are different degrees of deuteration of the same sample. Finally, we should mention that in a general way our observations on the effect on changing cations, anions and/or deuteration of the samples agree well with what was observed by Koralewski [1] in his previous work.

4. Energy gap calculations

MORD is a quite useful tool for determining band gaps in solids. It was first used for energy gap measurements in semiconductors by Ebina *et al* [10], Balkanski *et al* [11] and Balbin Villaverde and Donatti [12], to mention only some of the researchers working in this subject. This method for energy gap calculation was later extended to the case of insulators by Kase and Ohi [13], Khalilov *et al* [14] and Grevendonk *et al* [15].

For direct allowed optical transitions we have, according to Boswarva *et al* [16], the following relation between the Verdet constant of the solid and the photon energy of the incident light:

$$nV = K_2 F_2(x) \quad (3)$$

where n is the index of refraction of the material, V ($\text{min G}^{-1} \text{cm}^{-1}$) is the Verdet constant, K_2 is a constant independent of the frequency and $x = E/E_g$ with E being the incident photon energy and E_g the corresponding energy gap. The function $F_2(x)$ is given by the expression

$$F_2(x) = (1/x)[(1-x)^{-1/2} - (1+x)^{-1/2}] - 1. \quad (4)$$

This relation, known as the BHL formula, was derived from a quantum mechanical treatment of the Faraday rotation in semiconductors. A different expression was found by Kolodziejczak *et al* [17] and Roth [18] using only a semiclassical approach. This relation, currently referred to as the KLN formula, is given by the relation

$$nV = K_1 F_1(x) \quad (5)$$

where now the function $F_1(x)$ is a more complex relation between V and the photon energy:

$$F_1(x) = (1/x)[(1-x)^{-1/2} - (1+x)^{-1/2}] - (4/x^2)[2 - (1-x)^{1/2} - (1+x)^{1/2}]. \quad (6)$$

For any value of x the function $F_1(x)$ is always lower than $F_2(x)$; therefore the value for E_g obtained from the KLN formulae is always higher than that calculated from the BHL relation. The two formulae are very similar and both approach $(1-x)^{-1/2}$ when the incident photon energy comes close to the energy gap, i.e. when $E \rightarrow E_g$.

Table 3. Energy gaps E_g and the K -parameter for the eight KDP-type crystals calculated through the BHL method (equations (3) and (4)) and the KLN method (equations (5) and (6)). It also includes the energy gap E_g^{op} for each crystal obtained by optical dispersion.

Crystal	This work				Koralewski's work			
	E_g (eV)		K (min G ⁻¹ cm ⁻¹)		E_g^{op} (eV)	E_g (eV)		E_g^{op} (eV)
	BHL	KLN	BHL	KLN		BHL	KLN	
RDA	6.7	7.4	0.590	1.18	7.26	—	—	—
KDA	6.4	7.2	0.542	1.39	7.23	6.52	7.31	8.01
CDA	5.9	6.6	0.460	1.17	7.24	—	—	—
ADA	6.7	7.6	0.635	1.61	7.08	6.32	7.13	6.89
DRDA	5.8	6.5	0.428	1.06	7.46	—	—	—
DCDA	5.5	6.1	0.419	1.23	7.38	—	—	—
KDP	7.6	8.5	0.442	1.10	8.31	7.72	8.66	8.58
RDP	6.2	6.9	0.289	0.705	8.37	—	—	—

In the case of phonon-assisted transitions between the conduction and the valence bands, we must include also the phonon energy E_{ph} in the equations. Assuming a one-phonon emission and absorption process, Kolodziejczak *et al* [17] found the relation

$$nV = K_3 F_3(x') \quad (7)$$

where $x' = E/(E_g + E_{ph})$ and

$$F_3(x') = (1/x'^2) \ln[1/(1 - x'^2)] + (1/x') \ln[(1 - x')/(1 + x')] + 1 \quad (8)$$

while Boswarva *et al* [16] obtained the result

$$nV = K_4 F_4(x') = K_4 \left\{ \frac{1}{2} \ln[1/(1 - x'^2)] + (1/2x') \ln[(1 - x')/(1 + x')] + 1 \right\}. \quad (9)$$

These last two functions are quite different from F_1 and F_2 , rising more slowly, without diverging when E approaches E_g . The BHL and KLN formulae, although derived for the first time for semiconductors, were later successfully extended for insulators, giving also in this case values of E_g in fairly good agreement with those obtained from other methods, such as absorption spectra and optical dispersion.

From our Verdet constant dispersion data we calculated the values of E_g for all the samples by employing the BHL and the KLN formulae. We found that the difference between the values of E_g given by the two methods was in the range 10–15% for all the samples. Values of the index of refraction for our samples as a function of the wavelength were calculated using the dispersion relation for each crystal given in the work published by Kirby and DeShazer [9]. In table 3 we display the values of E_g obtained from both the BHL and the KLN methods, including also in this table the results published by Koralewski for three of the crystals: KDP, ADA and KDA. It can be seen that, for these last crystals, the difference between Koralewski's values and ours is only of the order of 1 eV for KDA and KDP and diminishes to 0.4 for ADA, which means that quite reasonable agreement was obtained. This agreement is more remarkable for ADA since that sample showed one of the highest errors for its Verdet constant measurement.

We also tried to fit our data using the function given in equations (8) and (9), which corresponds to the case of phonon-assisted transitions, but the values obtained for E_{ph} were physically unreasonable.

We display in table 3, for comparison, the values of E_g for each of our samples calculated from the ordinary refractive index dispersion data using the relation proposed by Wemple and DiDomenico [19]. The value of E_g calculated from optical dispersion will hereafter be denoted as E_g^{op} . According to the model of Wemple and DiDomenico, a plot of $(n^2 - 1)^{-1}$ against $1/\lambda^2$ should be a straight line, from which can be calculated the parameter E_0 (oscillator energy). E_g^{op} is related to E_0 by the approximate relation $E_0 \approx 1.5E_g^{\text{op}}$. We plotted $(n^2 - 1)^{-1}$ as a function of $1/\lambda^2$ for each of our samples using the data given by Kirby and DeShazer [9] for the ordinary index of refraction, restricting ourselves to only the linear portion of the plot, i.e. without taking into account the ultraviolet and the near-infrared data points which showed deviations from the fitted straight line. We should point out that the values obtained for E_g^{op} depend strongly on the source used for the index of refraction data, which explains the difference between our values for E_g^{op} and those given by Koralewski *et al* [2] for KDP, ADA and KDA. The E_g^{op} -values for five out of the eight crystals lie between the values for E_g obtained by the BHL and KLN formulae, or very close to them. Larger discrepancies are found for the two deuterated crystals DRDA and DCDA and for RDP; such a behaviour can be explained if we take into account that an error of only 1% in the measurement of the Verdet constant for the shortest wavelengths causes a shift in the value of E_g as high as 0.5 eV for the BHL fitting.

In spite of such an uncertainty in the calculated values for E_g we can conclude that, regarding the magnitude of the energy gap, the crystals that we studied could be divided into three groups: in the first group we have the deuterated crystals with the lowest values for E_g , followed by the arsenate family with intermediate values for E_g and finally in the last group are found the phosphates with the highest values of E_g . We shall recall that the same three groups were observed when we studied the average $\bar{\gamma}$ -values for our crystals.

Summarizing, we can say that the effect of the substitution of hydrogen by deuterium in the samples is to shift the band absorption edge to longer wavelengths; the same effect is observed when the anion H_2PO_4^- is substituted by H_2AsO_4^- .

We would like to remark that the MORD method allows us to obtain values for E_g in very good agreement with those found by other methods, even for the case, like ours, where the photon energy E is far from the energy gap E_g . Certainly, more accurate values of E_g could be obtained by using light sources in the ultraviolet with a photon energy much closer to the absorption edge.

Acknowledgments

We gratefully acknowledge the financial support of the Fundo de Apoio à Pesquisa of Universidade Estadual de Campinas, Financiadora de Estudos e Projetos of Brazil and Conselho Nacional de Desenvolvimento Científico e Tecnológico of Brazil, which made possible the completion of this work.

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