

Influence of cleavage in liquid helium on the shape of the $n=1$ exciton reflection band in KI and RbI crystals

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys.: Condens. Matter 6 2847

(<http://iopscience.iop.org/0953-8984/6/15/007>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.147

The article was downloaded on 12/05/2010 at 18:09

Please note that [terms and conditions apply](#).

Influence of cleavage in liquid helium on the shape of the $n = 1$ exciton reflection band in KI and RbI crystals

A A O'Connell-Bronin

Institute of Physics, Estonian Academy of Sciences, Tartu, Riia 142, EE-2400, Estonia

Received 28 July 1993, in final form 4 November 1993

Abstract. A noticeable change in the $n = 1$ exciton reflection band of KI and RbI crystals exposed to air was revealed after cleavage in liquid helium. This change is explained by disturbance of the near-surface layer by charged surface dislocations and other defects, which appeared after cleavage at a low temperature. A moderate irradiation by photons in the exciton region and/or heating leads to the removal of the disturbance and, correspondingly, to relaxation of the crystal surface.

1. Introduction

The method of cleaving crystals in liquid helium has been used to obtain a 'virgin' surface of the compounds under investigation and, correspondingly, to obtain the maximum information about the nature of excitons in crystals. For alkali halides the first experimental results obtained by this method were reported in 1971 by Petroff *et al* [1]. Later cleavage in liquid helium (CLH) was exploited by many researchers to study alkali halides [2–5]. The reason for this is that most of these compounds are hygroscopic. However, the problem of near-surface effects is rather complicated. Hopfield and Thomas [6] have introduced the concept of a 'dead' layer to explain the behaviour of excitons near the crystal surface [6]. Study of this problem has shown that the spectral properties of crystals depend on many factors: the intensity of the probe beam, the dose of irradiation, and the surface treatment [7–11]. The factors mentioned have mainly been determined by investigations of semiconductor crystals. Recently, in [12] a manifestation of the 'dead' layer in the $n = 2$ exciton region of the reflection spectrum (RS) of NaI crystals was reported. According to theory [7] the manifestation of similar effects in the $n = 1$ exciton region of alkali iodides should be insignificant, because the $n = 1$ excitons in these compounds are very 'deep', i.e. they have large binding energies. Nevertheless, in the present work, noticeable changes in the $n = 1$ exciton RS of KI and RbI crystals were revealed, which are due to the cleavage conditions, thermal treatment and irradiation of the crystal surface. The results obtained are compared with the data of Petroff *et al* [1] and Nishimura [4].

2. Experimental procedure

The samples were 6 mm×6 mm plates of perfect KI and RbI single crystals grown by the Kyropoulos method from zone-purified material (60 zones). To study the influence of the purity of crystals on the experimental results, part of the compounds were purified less carefully. Note that, although the crystals investigated are hygroscopic, they are much

smaller than NaI and LiI crystals. Therefore, before the experiment, the sample was cleaved in air and quickly placed into an immersion helium cryostat. Thereby, as noted in [13], contamination of the crystal surface was insignificant. Then the sample was cooled to liquid-helium temperature in about 1 h. Further the RSS from the surface cleaved in air were measured. Then CLH was performed and again the RSS were measured.

The cleaving wedge had the same shape as a medical scalpel. The cleavage was effected by a sharp blow. The experimental procedure is described here in detail because there are considerable differences between the RSS obtained by us and by other workers.

The source of exciting light was a deuterium lamp (400 W). Its light was passed through a double-prism monochromator (DMR-4) and focused on the sample surface by a lens. The use of narrow monochromator slits ensured that the probe beam had a comparatively weak influence on the surface properties of the sample. A special irradiation of the sample surface was carried out by exposure to the light passing through the monochromator with widely open slits. The reflected light was detected with a solar-blind photomultiplier (PhEU-142), which considerably weakened the share of the luminescence light from the visible region in the measured RS. The error of the monochromator scale was ± 2 meV. The spectral resolution was 1.2 meV.

3. Experimental results and discussions

In figure 1(a) the exciton RSS of KI obtained under different experimental conditions are presented. The full curve shows the RS of the surface cleaved in air ($T = 4.2$ K). It coincides well with the spectra obtained earlier by other workers [14, 15]. The classical shape of the dispersion contour is disturbed by the presence of a peculiarity on the high-energy side of the $n = 1$ band in the region of the longitudinal-transverse splitting. The broken curve shows the RS from the surface of the same sample after CLH. As can be seen from a comparison with the full curve, a considerable increase in the high-energy part of the RS contour takes place. The maximum and the minimum of the $n = 1$ band shift to the blue. On the low-energy side of the band the peculiarity coinciding in energy with the maximum of the reflection band in full curve was preserved. In a comparison of this result with the data reported earlier, note that Petroff *et al* [1] were the first to carry out CLH on alkali halides. In their work a RS of KI was presented ($T = 1.8$ K), which had a number of new peculiarities compared with the results of Baldini *et al* [14] obtained after cleavage *in situ* at 6 K (under high-vacuum conditions). However, no RS of KI from a surface cleaved in air was presented there. Further, Nishimura presented the RSS of KI without [15] and after CLH [4]. A comparison of these spectra shows that they coincide. However, the work reported in [4] was devoted mainly to the study of luminescence, which was performed using a monochromator with relatively wide slits. Therefore, it is not excluded that the sample surface in these experiments was preliminarily strongly irradiated. Note also that the reflection data Baldini *et al* [14] have been obtained with relatively wide slits (spectral resolution, about 5 meV). In figure 1(b) a comparison of our RS after CLH and those obtained by Petroff *et al* and by Nishimura is shown. As can be seen, Nishimura's RS coincides precisely with that obtained by us after cleavage in air, but the RS contour obtained by Petroff *et al* has essential differences. One of the causes of the differences in the spectra presented in figure 1(b) may be the effects of polarization introduced by using a double monochromator at an angle of less than 45° . However, our investigations in the case of NaI and LiI crystals [12, 16] showed that the RSS at near-normal incidence and 45° are almost identical. Note also the coincidence of the RSS obtained by Nishimura and by Baldini *et al*

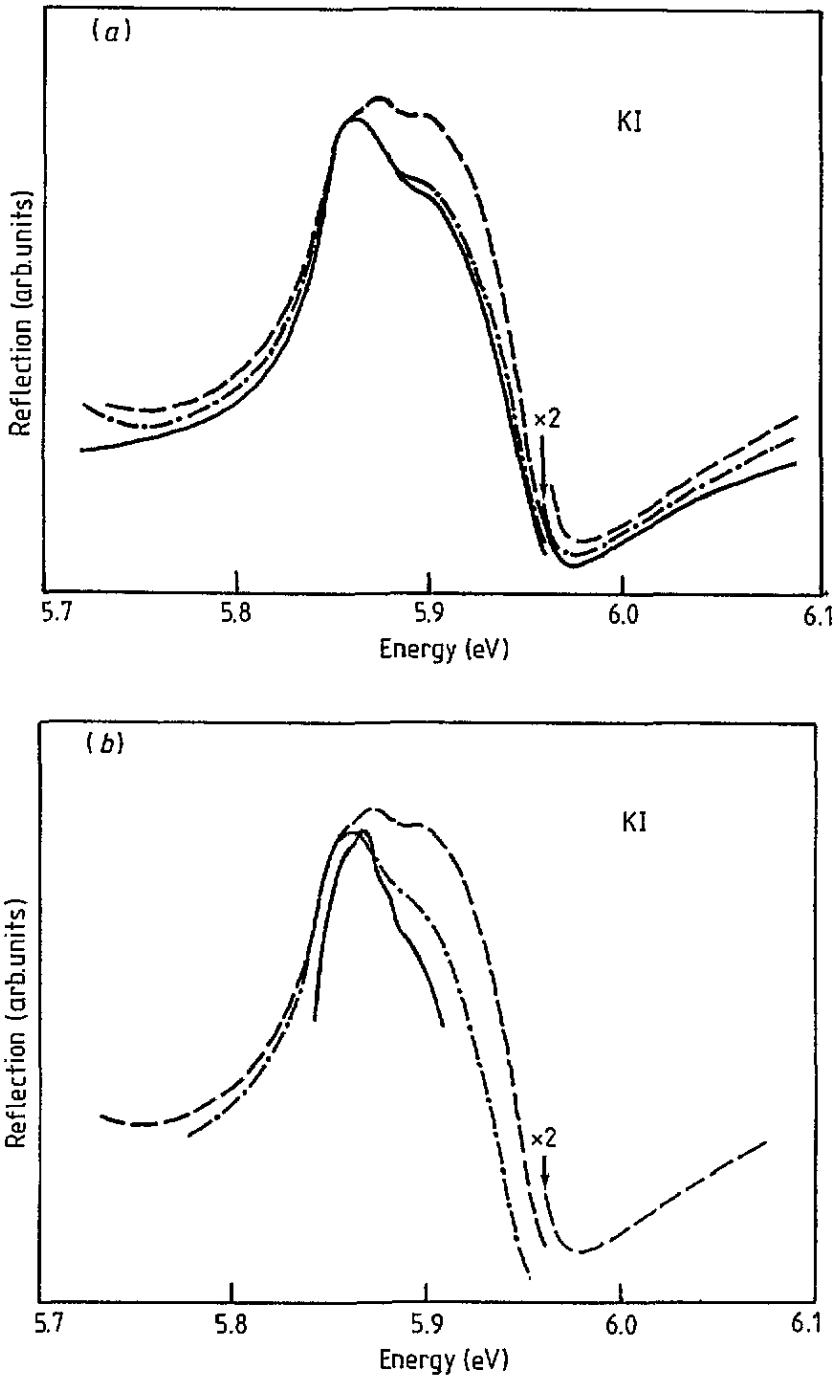


Figure 1. (a) Reflection spectra of KI crystals (incidence angle, 45° ; $T = 4.2$ K): —, cleaved in air; ---, after CLH; - · -, after subsequent irradiation by spectral light with a peak energy of 5.98 eV (minimum of rs) and an optical half-width of 0.05 eV for 10 min. (b) Reflection spectra after CLH: ---, our data; - · -, data obtained by Nishimura [4]; —, data obtained by Petroff *et al* [1]. All spectra are normalized to the rs maximum of the crystal cleaved in air.

using a single monochromator and ours measured before CHL. In figure 2 the RSs of RbI crystals before and after CLH are presented. They have differences analogous to those of KI.

In the course of investigation it was revealed that on irradiating a surface cleaved in liquid helium by a moderate dose of photons in the exciton energy region, the RS contour is transformed: it becomes almost precisely the same as it was before CLH (see dash-dotted curve in figure 1(a)). Furthermore, as can be seen in figure 3, the same change in RS occurs on heating the crystals. Thereby the subsequent cooling of the crystal to liquid-helium temperature will not restore the RS contour.

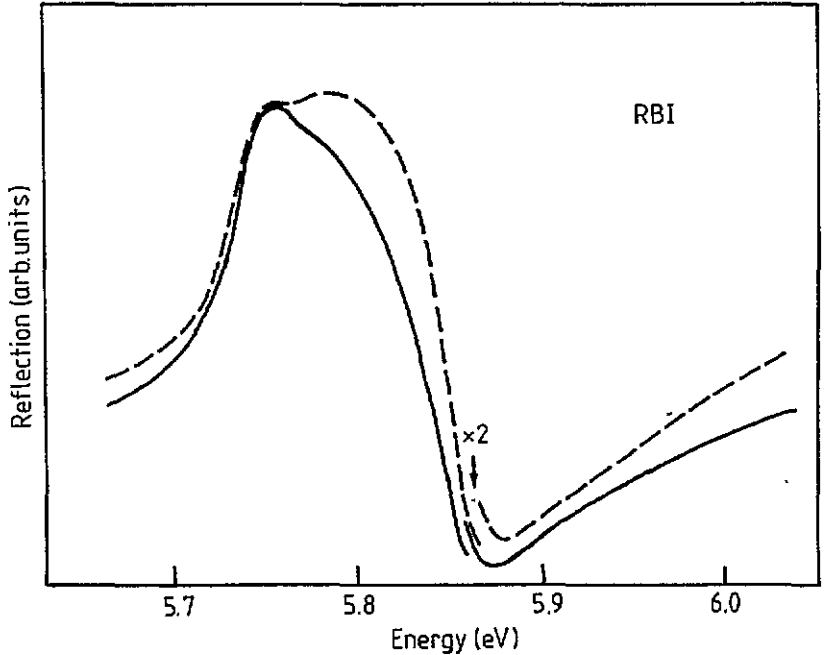


Figure 2. Reflection spectra of RbI crystals ($T = 4.2$ K) before (—) and after (---) CLH.

In most previous work [1–5], CLH has been used only as a tool to prevent contamination of the crystal surface. The first theoretical comparisons of the RSs of the crystals cleaved in liquid helium and exposed to air were reported by Schulthesis and Balslev [8] and by Travnikov [10]. To explain the difference between these crystals, the effects of a 'dead' layer and a near-surface electric field were used. The influence of surface irradiation and other effects on the sample surface were analysed. The results of such effects have been studied fairly widely in semiconductors [7–11]. For alkali halides, the first such investigation was made in the $n = 2$ exciton region [12]. In alkali halides, $n = 1$ excitons have a very large binding energy. Therefore, according to Evangelisti *et al* [7], for the disturbance and, in a limiting case, for the ionization of such excitons, a rather strong electric field is needed. Nevertheless, our results show a noticeable influence of the CLH on the shape of the $n = 1$ exciton band. It may be supposed that, after CLH near-surface exciton states appear, whose characteristics differ from those of volume states. As a result, the volume and near-surface excitons bands with different maxima manifest themselves simultaneously in the RS. Note

that the 'surface excitons' in alkali halides were proposed for the first time in 1973 by Kartheuser [17], on analysing the RS structure in the 2s exciton energy region, in particular, of KI crystals. In [8], it was assumed that in the near-surface layer of semiconductors after CLH, unlike the situation after cleavage in air, the magnitude of the electric field is very small. However, alkali halides are strongly ionic crystals. Therefore, after cleavage, a superfluous electric charge always appears near their surface. One of the sources for this charge may be charged dislocations. As has been shown in [18], at room temperature after rapid cleavage a very small number of surface dislocations appear because of their fast relaxation. Later it proved [19] that at low temperatures the dislocations appearing during cleavage remain frozen in the near-surface region. As a result the surface stays unrelaxed. In the present work it was observed that the experimental results do not depend on the purity of crystals. This to a certain extent testifies to the structural (dislocational) nature of the observed effects.

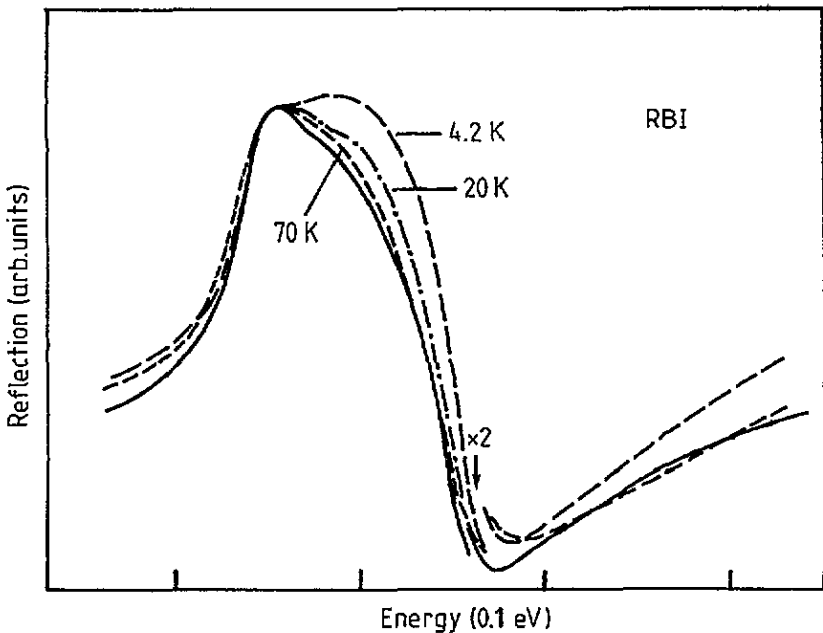


Figure 3. Contours of the reflection spectra of RbI crystals measured before CLH (—), after CLH (---) and at two temperatures during subsequent heating (— · —, $T = 20$ K; ---, $T = 70$ K).

In [7, 11] it has been shown that surface irradiation leads to compensation of the near-surface charge. Apparently, a similar process takes place in the case of KI and RbI crystals, leading to relaxation of their surface. Heating of the crystal also causes surface relaxation. One of the mechanisms for such surface annealing may be thermoactivated motion of charged defects in the crystal. In particular, in KI at $T = 15$ K the motion of charged I centres occurs [20]. At the same time it is known that at liquid-helium temperature these centres act as an obstruction to the motion of dislocations.

Thus, the main results of the present investigation call into question the widespread opinion that CLH forms an 'ideal' surface in alkali-halide crystals. In reality, even perfect cleavage at low temperatures has its own flaws in the form of surface dislocations and other

charges defects. In KI and RbI crystals, irradiation by photons in the exciton region and/or thermal annealing lead to surface relaxation.

Acknowledgment

The author is grateful to Professor Ch B Lushchik for useful discussions.

References

- [1] Petroff Y, Pinchaux R, Chekroun C, Balkanski M and Kamimura H 1971 *Phys. Rev. Lett.* **27** 1377
- [2] Plekhanov V G, Emel'yanenko A V and Grinfelds A U 1984 *Phys. Lett.* **101A** 291
- [3] O'Connel-Bronin A A 1986 *Fiz. Tverd. Tela* **28** 1005
- [4] Nishimura H J 1986 *J. Lumin.* **36** 75
- [5] Nishimura H, Saka Y, Nagata Sh, Hashimoto S, Okada T and Komatsu T 1987 *J. Phys. Soc. Japan* **56** 3715
- [6] Hopfield J J and Thomas D G 1963 *Phys. Rev.* **132** 563
- [7] Evangelisti F, Frova A and Patella F 1974 *Phys. Rev. B* **10** 4253
- [8] Schultheis L and Balslev I 1983 *Phys. Rev. B* **28** 2292
- [9] Schultheis L and Lagois J 1984 *Phys. Rev. B* **29** 6785
- [10] Travnikov V V 1985 *Zh. Eksp. Teor. Fiz., Pis. Red.* **42** 357
- [11] Kiselev V A, Novikov B V, Cherednichenko A E, and Ubushiev E A 1986 *Phys. Status Solidi b* **133** 573
- [12] O'Connel-Bronin A A and Treshchalov A B 1990 *Phys. Status Solidi b* **162** 289
- [13] Roessler D M and Walker W C 1967 *J. Opt. Soc. Am.* **57** 677
- [14] Baldini G, Bosacchi A, and Bosacchi B 1969 *Phys. Rev. Lett.* **23** 846
- [15] Nishimura H 1983 *J. Phys. Soc. Japan* **52** 3233
- [16] O'Connel-Bronin A A and Treshchalov A B 1989 *Phys. Status Solidi b* **154** 763
- [17] Kartheuser E P 1973 *J. Phys. C: Solid State Phys.* **6** L304
- [18] Gilman J J 1958 *J. Appl. Phys.* **29** 601
- [19] Golovin Yu I and D'yachek T P 1989 *Kristallografija* **34** 928
- [20] Vasil'chenko E A, Lushchik Ch B and Osmonaliev K 1986 *Fiz. Tverd. Tela.* **28** 1991