INVESTIGATION OF THE FUNDAMENTAL ABSORPTION OF LIGHT IN SINGLE CRYSTALS OF SODIUM NITRITE AND POTASSIUM IODATE IN THE REGION OF THE FERROELECTRIC PHASE TRANSITIONS

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Submitted to JETP editor August 1, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) **52**, 383-386 (February, 1967)

The spectral distribution of the fundamental absorption in $NaNO_2$ and KIO_3 is investigated in the region of the phase transitions. It is shown that the width of the forbidden band $E_g \simeq 0.02$ eV undergoes an abrupt change during the first-order phase transition in $NaNO_2$ at 160° C. An abrupt change $\Delta(dE_g/dT) \simeq 2.7 \times 10^{-4}$ eV/deg is observed during the phase transition in KIO_3 at 180° C; in the region of the phase transition at 65° C the change in E_g in KIO_3 is ~ 0.03 eV. According to previous thermodynamic calculations, these anomalies in KIO_3 are apparently due to a second-order phase transition at 180° C and to a first-order phase transition at 65° C.

THE anomalous behavior of the fundamental absorption edge in the region of the ferroelectric phase transition was first investigated in SbSI crystals.[1,2] The phase transition in SbSI at 22° C is accompanied by a jump in the width of the forbidden band E_g of about 0.06 eV. It has been shown from thermodynamic considerations[3] that this anomaly is characteristic of first-order phase transitions. In $BaTiO_3$ a jump of E_g of about 0.02 eV is observed[4] in the first-order phase transition from ferroelectric to the paraelectric phase. A jump of the temperature coefficient of the width of the forbidden band dE_g/dT should occur in the case of a second-order phase transition.[3] It has in fact been observed that a jump $\Delta(dE_g/dT)$ of about 10^{-4} eV/deg occurs at the Curie temperature in TGS and a corresponding jump $\Delta(dE_g/dT) \approx 3 \times 10^{-4}$ eV/deg occurs at the upper Curie point in Rochelle salt.

The study of the fundamental absorption of other ferroelectrics is useful in connection with the possibility of working out a convenient method of identification of phase transitions. In addition, this study is of interest from the point of view of an experimental check of the general relation between the width of the forbidden band of a crystal and its specific heat. In this work the fundamental absorption edge was investigated in $NaNO_2$ and KIO_3. Measurements of the specific heat of $NaNO_2$ were carried out by a number of authors,[6,7] whereas there are no data in the literature concerning the specific heat of KIO_3.

The investigation of the fundamental absorption of single crystals of $NaNO_2$ and KIO_3 was carried out on a SF-4A spectrophotometer. A specially constructed device for temperature measurements made it possible to control the temperature of the samples within a tenth of a degree. The spectral resolution of the monochromator was about 0.01 eV or better. The samples were in the form of platelets 1—2 mm thick. The measurements of the dielectric constant of the crystals were carried out with the aid of a UM-3 bridge.

According to the data which we obtained for $NaNO_2$ and KIO_3 the width of the forbidden band determined from the fundamental absorption edge is at room temperature ~ 3.14 and ~ 4.02 eV respectively. The fundamental absorption edge was obtained by extrapolating the logarithm of the optical density onto the wavelength axis. The investigation of the $NANO_2$ crystals was carried out both on samples with a ferroelectric cut (Y-cut according to the arrangement of Sawada and co-workers[8]) and on samples with a nonferroelectric cut. The temperature dependence of E_g for a Y-cut $NaNO_2$ crystal is shown in Fig. 1. Analogous dependences were obtained for all four investigated samples. In the ferroelectric and paraelectric regions the width of the forbidden band E_g changes linearly with the temperature with a coefficient $dE_g/dT \approx -(7.3 \pm 0.25) \times 10^{-4}$ eV/deg. A first-order phase transition accompanied by an abrupt anomalous decrease of E_g by $\Delta E_g \approx -0.02$ eV is observed at a temperature of 160° C. For samples of arbitrary (nonferroelectric) cut the jump at 160° C is $\Delta E_g \approx -0.015$ eV.

The temperature dependence of the width of the forbidden band for four samples of KIO_3 is shown

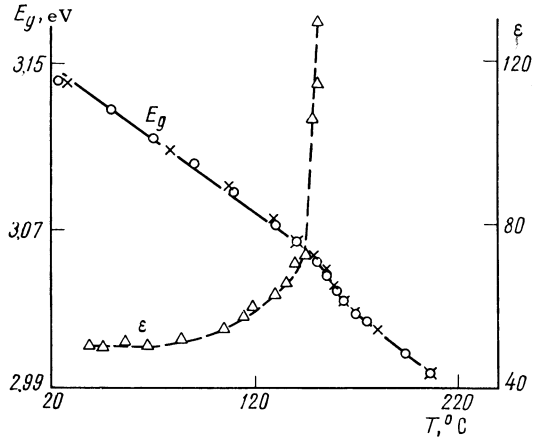

FIG. 1. Temperature dependence of the width of the forbidden band E_g and of the dielectric constant ϵ for $NaNO_2$ in the region of the phase transition; O—course of the curve for increasing temperatures, ×—course of the curve when the temperature is decreasing.

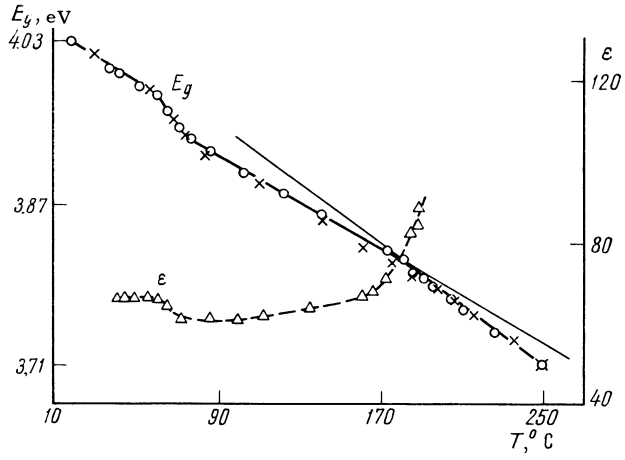

FIG. 2. Temperature dependence of the width of the forbidden band E_g and the dielectric constant ϵ for KIO_3 in the region of the two phase transitions (near 65 and 180°C); O—course of the curve when the temperature is increasing, ×—course of the curve when the temperature is decreasing.

in Fig. 2. The KIO_3 samples were cut from the most transparent portions of single-crystal octants perpendicular to the various directions of the edges of a pseudocube. Three sections in which the temperature change of E_g is linear can be discerned in the temperature dependence $E_g(T)$ for KIO_3 shown in Fig. 2. The temperature dependence of the width of the forbidden band exhibits two anomalies, at 65 and 180° C. At 65° C E_g decreases abruptly by ~0.03 eV. A break in the course of the temperature dependence $E_g(T)$ is observed at 180° C. Below and above 180° C, E_g changes linearly with the temperature with the coefficients $(dE_g/dT)_{ferro} \approx -(11.6 \pm 0.4) \times 10^{-4}$ eV/deg and $(dE_g/dT)_{para} \approx -(14.4 \pm 0.4) \times 10^{-4}$ eV/deg respectively. A second-order phase transition, accompanied by a jump of the temperature coefficient $\Delta(dE_g/dT) \approx -(2.8 \pm 0.8) \times 10^{-4}$ eV/deg, apparently takes place at 180° C, whereas the jump of E_g at 65° C is due to a first-order phase transition. This is in agreement with the data of Herlach [4] on the quadrupole spectra of KIO_3, who observed a first-order phase transition at 75° C and a second-order phase transition at 220° C.

The temperature dependences of the dielectric constants of $NaNO_2$ and KIO_3 are shown in Figs. 1 and 2. The results obtained confirm the existence of phase transitions near 65 and 180° C in the case of KIO_3 and near 160° C in the case of $NaNO_2$, and are in agreement with those of [10,11]. The phase transition in $NaNO_2$ was simultaneously investigated by recording of hysteresis loops. Hysteresis loops of single crystals of $NaNO_2$ were observed starting approximately from 120° C; the spontaneous polarization calculated from the hysteresis loops decreases sharply above 160° C, a fact which has already been noted previously in [10].

In accordance with the conclusions drawn on the basis of a thermodynamic calculation [3] and previously obtained results [1,2,4,5] which confirmed these conclusions, the optical data cited above not only confirm the existence of phase transitions in $NaNO_2$ and KIO_3, but also indicate their nature unambiguously.

In conclusion the authors express their gratitude to V. M. Fridkin for a discussion of the results and for help in the work.

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Translated by Z. Barnea
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