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THE INFLUENCE OF γ-IRRADIATION ON THE THERMOPHYSICAL PROPERTIES OF POTASSIUM AMMONIUM SULPHATE CRYSTALS

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The effect of γ-irradiation on the thermal properties of KNH_4SO_4 single crystals in the temperature range 300-600 K is investigated. The variation of C_p as a function of radiation dose is determined. Analysis of the results indicates that changes induced in the thermal behaviour of KNH_4SO_4 crystal by γ-irradiation might be due to direct collision with lattice atom and multiple atom displacement.

The presence of impurities and/or defects in crystals leads to various changes in their physicochemical properties. The changes induced may have a marked effect on the physical properties of the crystal and might even modify it for use as detectors and in thermal imaging applications [1-4]. Such defects of various types and distribution could be introduced in the crystals by several kinds of radiation.

Pure ammonium sulphate and mixed crystals of metal ammonium sulphate have been investigated quite thoroughly [5-12]. However, the problem of the nature of phase transition and the behaviour of NH_4^+ and SO_4^{2-} ions in the region of phase transition have not yet been solved. Moreover, the effect of irradiation on the thermal properties of such crystals have not been done according to our knowledge. In this work, some studies on the effect of γ-irradiation on thermal properties of KNH_4SO_4 single crystals in the temperature range 300-600 K are reported.

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Experimental

Single crystals of potassium ammonium sulphate were grown by slow evaporation from an aqueous solution of K_2SO_4 and $(NH_4)_2SO_4$ in equimolar ratio at temperature equals (313 K). To obtain single crystals of good quality, a small seed, from the single crystal already grown, was suspended in the saturated aqueous solution at 313 K. A small rotor was used to rotate the seed excentrically during the crystal growth. Chemical analysis and optical inspection were used as quality and purity control.

Specific heat C_p measurements were performed using a Shamadzu DSC TA30 thermal analyzer.

The measurements were done on 15-30 mg samples using a constant heating rate of 5-10 deg/min. The samples were γ-irradiated in air and at room temperature using a ^{60}Co gamma cell 220 manufactured by Atomic Energy of Canada Ltd. The used dose rate was $1.4 \cdot 10^5$ Rad/min. The specific heat C_p of irradiated samples with different dose up to 0.6 MRad was determined.

Results and discussion

Differential scanning calorimetry traces for non-irradiated a well as irradiated KNH_4SO_4 crystals in the temperature range 300-600 K were used to obtain the temperature dependence of the specific heat of KNH_4SO_4 crystals as shown in Fig. 1. It is clear from Fig. 1 that for all samples, the C_p *vs.* T curves exhibit anomalies. The anomalea occurs over a relatively wide temperature range instead of abrupt changes in the vicinity of the phase transition.

This behaviour might be due to the fact that KNH_4SO_4 contains two kinds of NH_4^+ and one kind of SO_4^{2-} ions in paraelectric and ferroelectric phases. These ions are distorted from tetrahedral symmetry in both phases and are accompanied by electric dipole moment [13]. The K^+ ions tend to replace the NH_4^+ (II) rather than the NH_4^+ (I) ions and hence broaden the transition and transform it into transition close to second order [9, 14]. The considerably large excess of heat capacity of KNH_4SO_4 crystals, which was observed in a wide temperature range, has been interpreted recently as due to the inter-chain interaction [15].

Gamma irradiation will induce certain defects in the crystals and every domain wall could be considered as a sort of imperfection. Moreover, the local strain in the vicinity of the local damaged centre will cause greater disturbance than any induced impurity. Gamma irradiation affects the transition temperature T, as well as the values of C_p at transition.

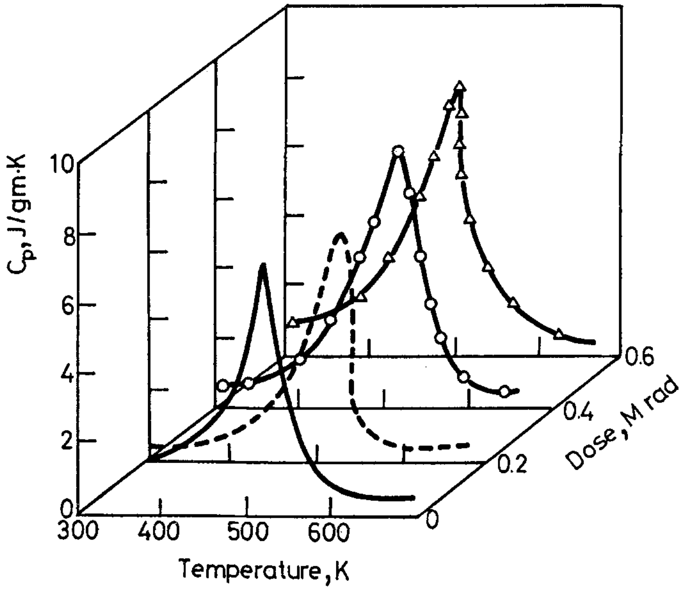

Fig. 1 Temperature dependence of the specific heat Cp of KNH_4SO_4 crystals for different γ-radiation dose: —— 0, - - - 0.2, ○ 0.4, Δ 0.6 MR

The behaviour of Tc and Cp at transition as functions of radiation dose are shown in Fig. 2. The value of Tc increases while that of Cp at transition decreases with increasing irradiation dose up to about 0.2 MR. Then, as the radiation does increases, Cp at transition increases reaching a value of ≈ 7.8 J/g·K at 0.6 MR while Tc decreases reaching a minimum value of ≈ 505 K at 0.6 MR. This behaviour of Cp could be due to the fact that γ-irradiation affects the release of charge carriers as well as the trapping process.

At low exposure, however, the trapping process is assumed to be negligible and the increase in carrier concentration needs more thermal energy to enhance their effect on Cp. Hence, the induced specific heat Cp as a function of exposure dose reveals a minimum at an optimum dose near 0.2 MR.

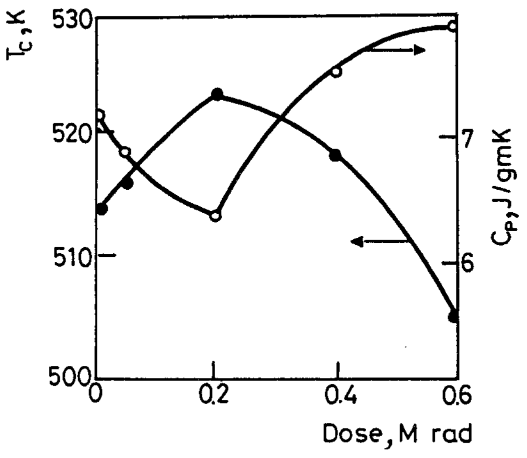

Fig. 2 Variation of T_c and C_p at transition with γ-radiation dose for KNH_4SO_4 crystals

Since the temperature dependence of the specific heat near the phase transition is close to second order, as mentioned earlier, then it obeys an experimental law [9]:

$$\Delta C_p = Z\,(Nu^2/RT^2)\exp(-u/RT) \qquad (1)$$

where N is the number of atoms displaced from the equilibrium position, u is the activation energy; R is the universal gas constant; Z is the coordination number, i.e. the number of neighbours of each atom.

Figure 3 shows the dependence of $\ln(\Delta C_p T^2)$ on 1/T for irradiated as well as un-irradiated crystals. It is clear that the experimental points could be approximated by straight lines with the exception of a temperature interval in the vicinity of the transition. The slopes of the straight lines give the activation energies which are listed in Table 1. The number of atoms displaced from the equilibrium position (N) could be obtained from the intersection of the lines. Taking $Z = 4$ for the crystal [11], the values of N for the samples are estimated and given in Table 1.

The data given in Table 1 confirms again that γ-irradiation induces defects in the crystal. The maximum change in the number of displaced atoms is $\approx 1.9\cdot 10^8$ for a radiation dose of ≈ 0.2 MR.

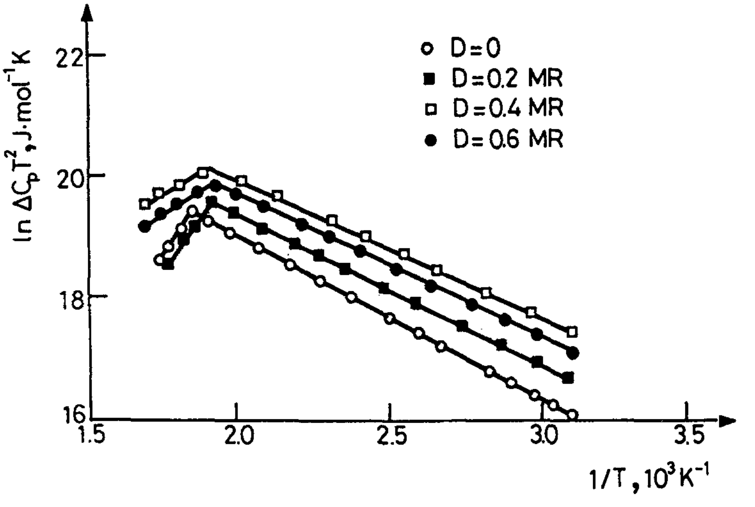

Fig. 3 Dependence of ln (ΔC_pT^2) on $1/T$ of KNH_4SO_4 crystals for different γ-radiation dose: (D)

Table 1

Dose, M Rad	u, J/mole	N
0	24.23	$1.26 \cdot 10^8$
0.2	19.55	$3.2 \cdot 10^8$
0.4	23.01	$1.89 \cdot 10^8$
0.6	28.10	$2.09 \cdot 10^8$

From this work, it is established that γ-irradiation changes T_c, broadens the transition and transforms it into transition close to second order.

* * *

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Zusammenfassung — Es wird der Einfluß von Gammaeinstrahlung auf die thermischen Eigenschaften von KNH_4SO_4-Einkristallen im Temperaturbereich 300-600 K untersucht. Die Änderung von C_p wurde als Funktion der Strahlungsdosis bestimmt. Eine Analyse der Ergebnisse zeigt, daß die gammastrahlungsbedingten Veränderungen im thermischen Verhalten von KNH_4SO_4-Kristallen einer direkten Kollision mit Gitteratomen und einer mehrfachen Verlagerung von Atomen zugeschrieben werden kann.