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EFFECTS OF AN ADMIXTURE AND FAST NEUTRON IRRADIATION ON THERMAL PROPERTIES OF SODIUM POTASSIUM SULPHATE CRYSTALS

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The differential thermal analysis curves and the specific heat at constant pressure, C_p, of pure and Cu^{2+}-doped sodium potassium sulphate crystals were studied. Different neutron fluences were used up to 2.6×10^{10} n/cm^2, in the temperature range 300–500 K. Impurity incorporation generally increased the specific heat up to a maximum at 5% Cu^{2+} content. The peaks for the doped crystals were shifted to lower temperature as a result of neutron irradiation. This behaviour is discussed on the basis of defects induced by irradiation.

It is well known that foreign ions present as defects in a crystal lattice enhance phonon scattering. A measure of this enhancement is provided by the change in the specific heat referred to that of the pure crystal [1].

Crystalline sodium potassium sulphate, $NaKSO_4$, is a member of the family of double sulphate crystals. Their importance arises from the fact that some double sulphate crystals display ferroelectric and ferroelastic behaviour in different temperature ranges [2–5]. Studies of these ferroelectric and ferroelastic materials are important for their use as piezoelectric components and pyroelectric detectors, and in the memory of computers [6–8].

Sodium potassium sulphate crystals possess orthorhombic symmetry at 300 K and belong to an mmm point group [9].

Electrical conductivity measurements [10] on pure and doped fused samples of $NaKSO_4$ reveal high ionic conductivity values in the high-temperature range. The order-disorder transitions and solid-state kinetics of this compound have also been studied [11], as have the thermal, electrical and elastic properties, together with the effects of neutron irradiation on pure samples [12–16].

The aim of the present work was to study the effects of doping with Cu^{2+} on the specific heat, C_p, and DTA curves, and also the effects of fast neutron irradiation on $NaKSO_4$ crystals.

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Experimental

Sodium potassium sulphate crystals were grown isothermally at 315 K from aqueous solution. The initial substances used for the synthesis of $NaKSO_4$ were of chemical grade purity. The $NaKSO_4$ for crystal growth was subjected to five-fold slow recrystallization from water. Doped crystals were grown from aqueous solutions containing $CuSO_4 \cdot 5H_2O$ in concentrations of 1, 2, 5 and 10 per cent by weight. Chemical analysis, X-ray diffraction and optical inspection were used for purity control and to ensure the quality of the crystals.

The specific heat under constant pressure, C_p, was determined by using a differential scanning calorimeter (DSC) technique, a Heraeus DSC cell being connected to a Heraeus DTA 500 thermal analyser. Measurements were performed by applying the base line method [17]. Lidded pans, made of aluminium, were used to eliminate the slope of the base line. A Pt 100 thermocouple was used as a temperature sensor, and a heating rate of 2 deg per min was applied.

The samples were irradiated with different neutron fluences at room temperature (298 K), using a compact D–T neutron generator (Philips product Pw 5310) with known neutron spectrum [18]. The neutron flux in each run was controlled by using

Table 1

Element	Abundance, %	Reaction and products	Type of decay	Decay product	Activity per g target	Energy of gamma, MeV	Half-life
$^{32}_{16}S$	95.06	(n, p)$^{32}_{15}P$	β^-	^{32}S	43 Bq	—	14.3 day
$^{34}_{16}S$	4.2	(n, α)$^{31}_{14}Si$	β^-	^{31}P	46 Bq	1.266	2.6 hr
$^{41}_{19}K$	6.91	(n, γ)$^{42}_{19}K$	β^-	^{42}Ca	2 Bq	1.525	12.4 hr
		(n, p)$^{41}_{18}Ar$	β^-	^{41}K	45 Bq	1.29	1.8 hr
		(n, α)$^{38}_{17}Cl$	β^-	^{38}Ar	18 Bq	2.168	37.3 min
$^{63}_{29}Cu$	69.1	(n, 2n)^{62}Cu	β^+	^{62}Ni	687 Bq	0.51	9.73 min
$^{65}_{29}Cu$	30.9	(n, 2n)^{64}Cu	β^- (40%) β^+, EC (60%)	^{64}Zn ^{64}Ni	229 Bq	1.34	12.7 hr
		(n, p)^{65}Ni	β^-	^{65}Cu	11 Bq	1.48	2.52 hr

Cu foils as a monitor through the ^{63}Cu (n, 2n) ^{62}Cu reaction. A neutron beam with energy 14.5 MeV and flux 6×10^5 n cm^{-2} s^{-1} was used up to 12 hours of irradiation.

Results and discussion

Table 1 and Fig. 1 show the activities produced on the neutron irradiation of $NaKSO_4$ + Cu 10%. Differential thermal analysis curves are given in Figs 2 and 3. The structural phase transformation for $NaKSO_4$ crystals doped with different Cu^{2+} contents exposed to fluences of 1.7×10^{10} and 2.6×10^{10}n/cm^2 is a sharp one and occurs over a narrow temperature range. At a Cu^{2+} content of 2%, the peak is shifted towards lower temperature and another peak appears. At a neutron fluence of 1.7×10^{10} n/cm^2, as the Cu^{2+} content increases, the heat of transition ΔQ increases. It is also clear from Figs 2 and 3 that, as the neutron fluence increases, the peaks are shifted slightly to higher temperature.

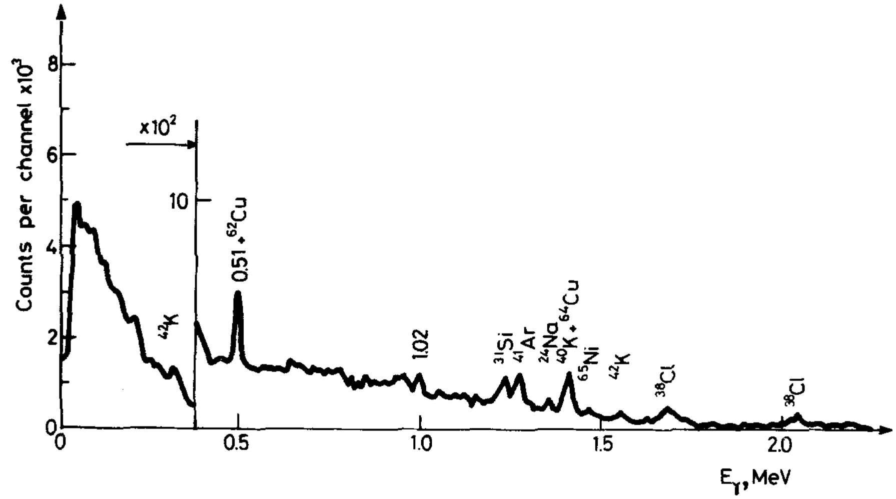

Fig. 1 γ-spectrum of irradiated Cu^{2+}-doped $NaKSO_4$ sample, recorded over 2000 s

The curves in Fig. 4 illustrate the temperature-dependence of C_p for $NaKSO_4$ with different Cu^{2+} contents at a neutron fluence of 1.7×10^{10} n/cm^2. It is clear that the value of C_p changes sharply with the Cu^{2+} content and exhibits a maximum at a Cu^{2+} concentration of 5%. The relatively strong increase in the specific heat of $NaKSO_4$ containing admixtures of foreign ions suggests the possibility of a formal approach to such crystals as two-phase systems, at a Cu^{2+} content of 5%, in which

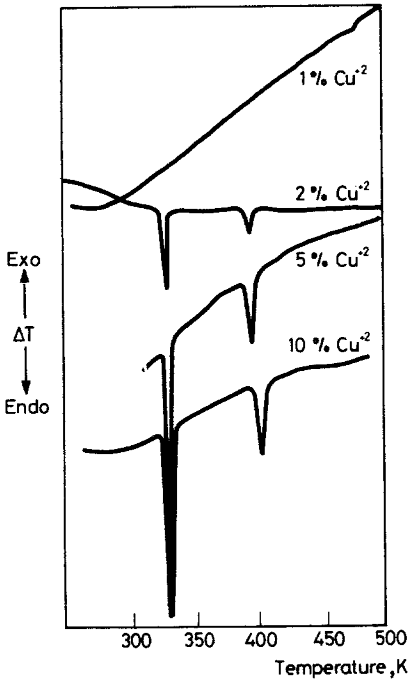

Fig. 2 Thermal analysis curves for $NaKSO_4$ samples with different Cu contents at a neutron fluence of 1.7×10^{10} n/cm^2

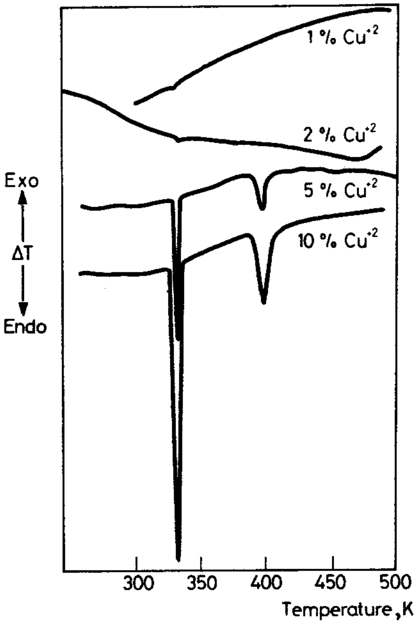

Fig. 3 Thermal analysis curves for $NaKSO_4$ samples with different Cu contents at a neutron fluence of 2.6×10^{10} n/cm^2

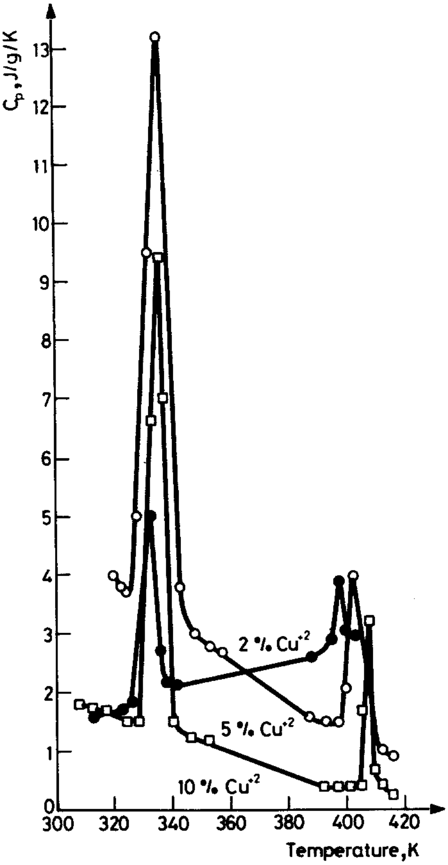

Fig. 4 Temperature-dependence of the specific heat at constant pressure, C_p, for different copper contents in $NaKSO_4$ crystals at a neutron fluence of 1.7×10^{10} n/cm^2

one phase consists of the perfect crystal lattice of $NaKSO_4$, and the other of spherical or cubic regions of the lattice distorted by the presence of the foreign Cu ions. The specific heat is different in the two phase. It is clear from Fig. 5 that at a Cu^{2+} content of 10%, as the neutron fluence increases, the walue of C_p increases too, but the peak temperature is shifted (a few degrees) towards higher temperature for the low-temperature phase and to lower temperature for the high-temperature phase. This behaviour can be attributed to the fact that an inhomogeneous strain is induced as a result of the stress produced by the presence of foreign ions.

Figure 6 shows the variation in C_p, measured around the phase transition temperature (t_c = 453 K), with the Cu content. It is seen from the Figure that the value of C_p increases sharply at low copper content, up to a maximum value of

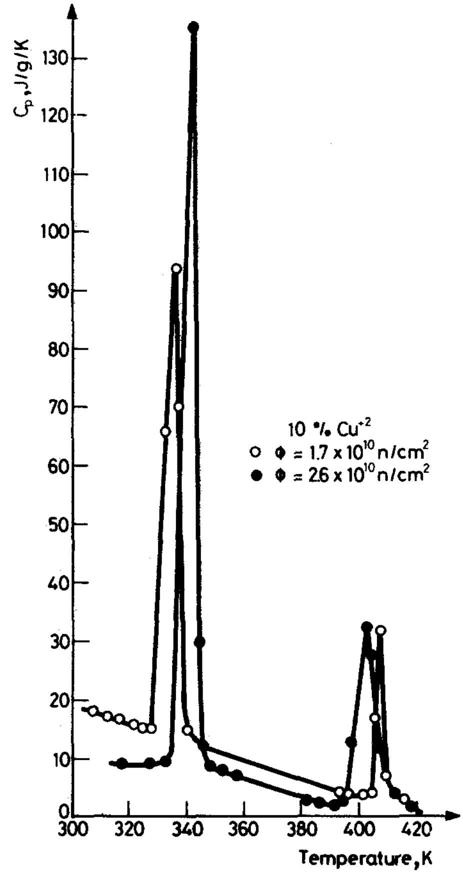

Fig. 5 Temperature-dependence of the specific heat, C_p, for 10% Cu^{2+} $NaKSO_4$ crystal irradiated with 1.7×10^{10} and 2.6×10^{10} n/cm^2

about 4 J/g/deg, and then decreases. This can be explained according to the previous theoretical results [19], which prove that defects can produce the drastic change in the critical behaviour.

From the above studies, it may be concluded that both implanted and original defects can really change the critical behaviour, masking the intrinsic properties of the crystals.

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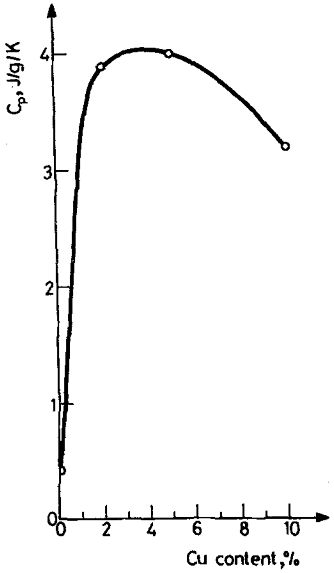

Fig. 6 Variation of C_p, measured around the phase transition temperature, with Cu content in $NaKSO_4$ crystals

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Zusammenfassung — Es wurden die DTA-Kurven und die spezifische Wärme bei konstantem Druck C_p von reinen, mit Cu^{2+} versetzten Natriumkaliumsulfatkristallen untersucht. Im Temperaturbereich 300–500 K wurden verschiedene Neutronenströme bis zu $2{,}6 \times 10^{10}$ n/cm^2 verwendet. Der Einbau von Verunreinigungen erhöht im allgemeinen die spezifische Wärme bis zu einem Maximum bei einem Cu^{2+} Gehalt von 5%. Im Ergebnis der Neutronenbestrahlung verschieben sich die Peaks für die versetzten Kristalle in Richtung niedrigerer Temperaturen. Dieses Verhalten wird auf der Basis strahlungsinduzierter Defekte besprochen.

Резюме — Измерены ДТА кривые и удельная теплоемкость C_p при постоянном давлении для чистых и легированных медью кристаллов сульфата калия. В температурной области 300–500 K был использован поток нейтронов мощностью до $2{,}6 \cdot 10^{10}$ n/см^2. Введение легированной примеси приводило к увеличению удельной теплоемкости до максимального значения при содержании меди равным 5%. Температурные пики для легированных кристаллов сдвигались в область более низких температур, вследствии облучения их нейтронами. Такое поведение их обсуждено на основе дефектов, вызванных облучением.