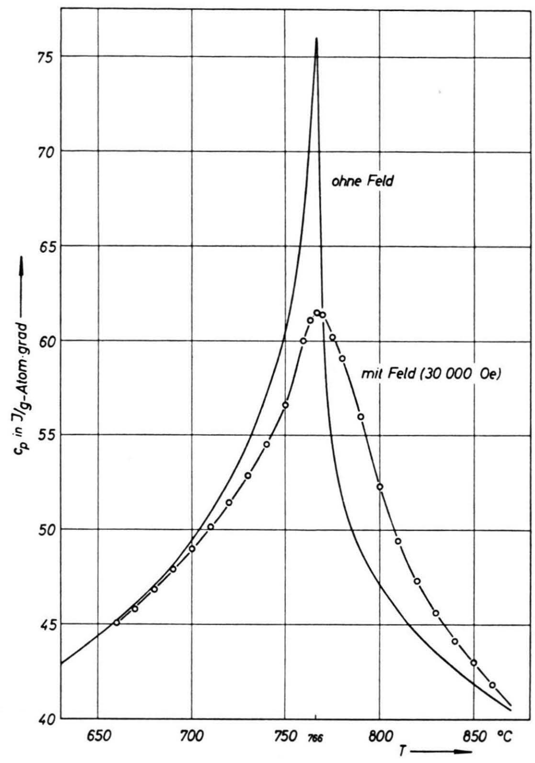

Abb. 1. Spezifische Wärme des Eisens in der Umgebung des CURIE-Punktes mit und ohne Magnetfeld (Chemische Zusammensetzung in Gew.-Proz.: 99,97 Fe; 0,009 C; 0,001 Si; 0,0005 Mn; 0,003 P; 0,004 S; 0,002 Al; 0,0029 O und 0,002 N).

die adiabatische Magnetisierung bzw. Entmagnetisierung zustande kam, für 1 bis 2 Minuten konstant blieb. Die Meßergebnisse sind in Tab.1 zusammengestellt. Mit Hilfe dieser Werte und der spezifischen Wärme $c_{p,0}$ ohne Feld wurde gemäß Gl. (3) die spezifische Wärme $c_{p,H}$ bei einem konstanten äußeren Magnetfeld berechnet. In Abb. 1 sind die beiden spezifischen Wärmen in der Umgebung des CURIE-Punktes miteinander verglichen.

Es ist offensichtlich, daß zwischen der spezifischen Wärme $c_{p,H}$ bei konstantem äußeren Feld und den magnetischen Eigenschaften eines Stoffes ein enger Zusammenhang besteht. Thermodynamische Betrachtungen von HIRSCHLER[4] zeigen, daß es bei der Kenntnis der Größe $c_{p,H}$ gelingt, einige Schwierigkeiten zu beseitigen, die auftreten, wenn man die spontane Magnetisierung von der wahren Magnetisierung zu trennen versucht.

Unter dem Einfluß eines äußeren Magnetfeldes wird die spezifische Wärme als Funktion der Temperatur in der Umgebung des CURIE-Punktes zu einer glatten Kurve, die keine Spitze am CURIE-Punkt hat, sondern ein Maximum, das bedeutend niedriger liegt. Die Spitze in der $c_{p,0}-T$-Kurve tritt bei der gleichen Temperatur auf, bei der die Kurve des magneto-kalorischen Effektes die größte Steigung hat.

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Thermoelectric Power of Solid and Molten Copper and Silver Iodide

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The thermal emf of molten silver iodide and solid and molten cuprous iodide has been measured using reversible electrodes. The results can be described by the following equations[1]

Molten AgI: $-\varepsilon=(489.8\pm2.8)\,\mu\text{V}/^\circ\text{C}$ $(560-650\ ^\circ\text{C})$,
Molten CuI: $-\varepsilon=(507.4\pm6.4)\,\mu\text{V}/^\circ\text{C}$ $(610-710\ ^\circ\text{C})$,
Solid CuI: $-\varepsilon=(1066.3-0.762\,t_{\text{m}})\,\mu\text{V}/^\circ\text{C}$ $(450-590\ ^\circ\text{C})$.

ε is the SEEBECK coefficient and t_{m} is the mean temperature of the salt column. The thermal emf of molten CuBr was found to be about 470 μV/°C. The change of the emf at the melting point is small in CuI and AgI. The "entropy of transfer" increases with increasing ratio of the radii of the anion and the cation in silver and cuprous halides.

If the entropy of the electron in the electrode is neglected, the thermoelectric power of a thermocell with reversible metal electrodes can be written[2]

$$\varepsilon F=S_{\text{M}}-\overline{S}_{\text{M}^+}-S^*_{\text{M}+}. \tag{1}$$

F is FARADAY's constant, ε the SEEBECK coefficient, S_{M} the molal entropy of the metal, $\overline{S}_{\text{M}^+}$ the partial molal entropy of the ion M^+ in the salt and $S^*_{\text{M}+}$ "the entropy of transfer" of the ion M^+.

Since the entropy of a single ion in a molten salt is not directly measurable, the physical meaning of the term $S^*_{\text{M}+}$ is unclear. Rather little attention has been taken to $S^*_{\text{M}+}$. PITZER[3] has only pointed out that the entropy of transfer of the cation is small, since the ion presumably is free to migrate through the salt without large activation energy.

The entropy of the ion M^+ in a simple binary salt can be estimated from the equation[3, 4]

$$\overline{S}_{\text{M}^+}=\tfrac{1}{2}\left(S_{\text{MX}}+\tfrac{3}{2}\,R\ln m_{\text{M}^+}/m_{\text{X}^-}\right). \tag{2}$$

S_{MX} is the entropy of the salt and m_{i} is the atomic weight of component i.

[1] All stated errors in this paper are standard deviations.

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If this equation is valid, the entropy of a certain ion must be the same in all MX salts. The molal entropies of AgCl, AgBr and CuCl at 900 °K are compiled by Kelley [5]. A calculation of the partial molal entropies of the anions and cations in these salts gives, Ag^+ in AgCl 23.20 cal./mole, degr., Ag^+ in AgBr 23.15 cal./mole, degr., Cl^- in AgCl 19.87 cal./mole, degr. and Cl^- in CuCl 19.74 cal./mole, degr. Eq. (2) thus seems to be a good approximation for the cuprous and silver halides. We have used the value 23.17 cal./mole, degr. for the partial molal entropy of the silver ion in silver iodide and 21.50 cal./mole, degr. for the partial molal entropy of the copper ion in the cuprous halides.

We have measured the thermoelectric power of molten and solid CuI, molten AgI and CuBr. The thermal emf of solid AgI has recently been published by Kvist [6], of CuCl by Nichols and Langford [7], of molten and solid AgBr by Ruch and Dupuy [8] and of molten AgCl by Senderoff and Bretz [9].

Experimental

The Supremax cell, which has been previously described, was used with small modifications [10]. Completely leak-free silver and copper electrodes were obtained by using narrow protection tubes of Alsint (sintered Al_2O_3).

Commercial AgI (Hopkin & Williams), CuI (Merck) and CuBr (Riedel de Haën) was used without further purification. All measurements were performed in argon atmosphere. CuI is stable in argon atmosphere to 920 °C [11] and no decomposition was observed in molten AgI to 650 °C. CuBr decomposes slightly and for this reson only a rough value of the emf could be obtained.

The emfs were measured with a Croydon potentiometer bridge, model P3.

	$-\varepsilon$ µV/°C	Standard deviation µV/°C	Temperature interval °C
Molten AgI	489.8	2.8	560 – 650
Molten CuI	507.4	6.4	610 – 710
Solid CuI	$1066.3 - 0.762\, t_m$	6.6	450 – 590
Molten CuBr	470	—	625

Table 1. The thermoelectric power of AgI, CuI and CuBr as a function of temperature.

Results and Discussion

The results are summarized in Table 1. The change of the emf at the melting point is small both in CuI and AgI, which is the case also for silver bromide [8]. All these salts are cubic at the melting points. The change of the emf in AgBr at the melting point has recently been discussed by Dupuy [12].

By using $\bar{S}_{M^+}$ from Eq. (2) we have calculated S^*_{M+} for the silver and cuprous halides (Table 2).

For the silver and the cuprous halides S^*_{M+} is apparently increasing with the ratio of the radii of the anion r_{an} and the cation r_{cat} and approximately proportional to $r_{an}/r_{cat} - 1$.

This is however not the case for silver nitrate and silver sulfate. ε and S^*_{M+} are low in these salts, which indicates that the silver ions are more strongly bound to the anions than in the halides.

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	S_{MX} cal./mole, degr.	$\bar{S}_{M^+}$ cal./mole, degr.	S_M cal./mole, degr.	$-\varepsilon$ µV/°C	S^*_{M+} cal./mole, degr.	$\frac{r_{an}}{r_{kat}} - 1 = k$	S^*_{M+}/k cal./mole, degr.
AgCl	43.07	23.20	17.24	375	2.68	0.44	6.09
AgBr	45.43	23.15	17.24	440	4.23	0.55	7.69
AgI		(23.17)	17.24	490	5.36	0.71	7.55
CuCl	41.24	21.50	14.86	436	3.41	0.89	3.83
CuBr		(21.50)	14.86	470	4.19	1.03	4.07
CuI		(21.50)	14.86	507	5.04	1.25	4.03

Table 2. S^* of the silver and cuprous halides at 900 °K.

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