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REGULARITIES IN MELTING POINTS OF LITHIUM HALIDES: IS LiH ANOMALOUS?

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Using experimental data for the melting temperature T_m for four Li halides (F to I), it is demonstrated that $T_m Z^{1/3}$ is close to constant, $\cong (2530 \pm 250)$ K, where Z is the atomic number of the halogen. This formula is not appropriate for what sometimes is considered the simplest halide, LiH, and therefore alternatives are investigated which involve a characteristic electrostatic energy $e^2/\epsilon s$, with s the internuclear separation and ϵ the static dielectric constant.

Keywords: Characteristic electrostatic energy; Dielectric constant

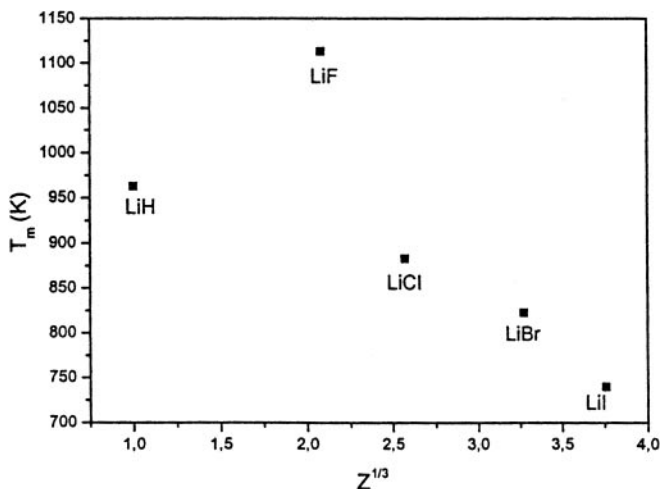
There is current interest in nuclear energy production via sonoluminescence of deuterated liquids. Thence we have surmised upon the possibility of sonicating molten lithium deuteride [1], where boosted efficiency might conceivably be obtained via chain reaction: for ${}^6\text{Li}$ hit by a neutron gives tritium and α , with the tritium then readily fusing with D to produce much energy, and another neutron. (Moderation of the reaction could be achieved with admixture of ${}^7\text{Li}$ or ${}^1\text{H}$.) This has motivated us to consider further the melting of LiD, and in particular whether it decomposes before melting. In fact, LiD and the closely similar LiH have very similar melting points [2] near 900 K (at atmospheric pressure) with decomposition over 200 K higher.

More generally we here consider the question of the behavior of the experimental melting temperatures T_m of the lithium halides LiF, LiCl, LiBr, LiI interpreting also the hydride LiH as a halide. To this end, we record in Table I the measured values of T_m in K for these five crystalline materials [3]. Since, in the original form of modern density functional theory, namely the Thomas–Fermi statistical method [4], the “size” of an atom is proportional to $Z^{-1/3}$, with Z the atomic number, we have entered in the final column of Table I the product $Z^{1/3}T_m$. Whereas the melting temperatures of the four halides F–I vary by a factor a little less than 2, the product is constant at a value 2530 K to within an error 10%. As seen from Table I, LiH is anomalous in this context.

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TABLE I Measured melting temperatures correlated with $Z^{-1/3}$

	T_m (°K)	Z	$Z^{1/3}T_m$ (°K)
LiH	963	1	963
LiF	1113	9	2315
LiCl	883	17	2269
LiBr	823	35	2691
LiI	740	53	2780

FIGURE 1 Melting points (in K) versus $Z^{1/3}$.

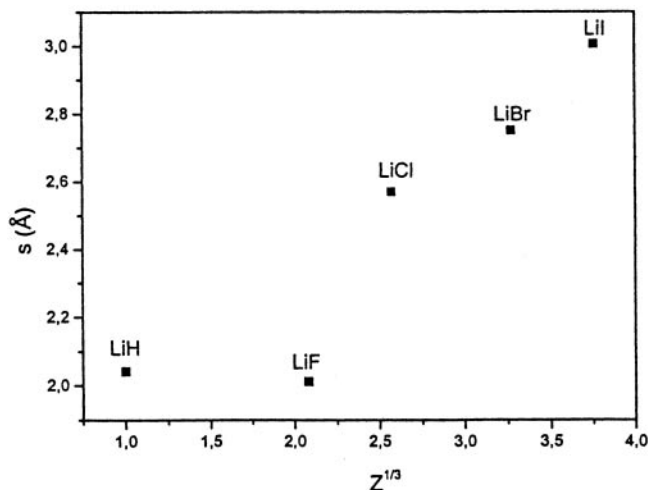
However, the same data depicted in Fig. 1 in the form of a plot of T_m versus $Z^{1/3}$, could lead to the different conclusion that it is LiF which is anomalous. To understand this, as a guide to the eye, the points for the Li salts of H, Cl, Br, and I can be joined by a smooth curve which then may be extrapolated to $Z^{1/3} = 0$. The $Z = 0$ value for T_m thereby found is $\cong 980$ K, whence if we associate this with a face-centered cubic form of Li solid at the appropriate lattice spacing and use the empirical relation $E_v/k_B T_m \sim 10$ where E_v is the vacancy formation energy [5], then one finds $E_v \sim 0.8$ eV which seems plausible. It is relevant in the above context that Barr and Lidiard [6] also correlated $k_B T_m$ with defect energies in ionic crystals. Thence with this rationalization in hand Fig. 1 might lead one to the conclusion that it is LiF which is the anomalous material.

To attempt to resolve this apparent conflict between the plot in Fig. 1 and the results recorded in Table I, we have considered a different approach, in which the thermal energy $k_B T_m$ associated with the melting temperature is compared with a characteristic Coulomb energy $E_C = e^2/\epsilon s$, where ϵ is the low-frequency dielectric constant [2,7,8] and s is the equilibrium internuclear separation [9]. Table II records values of ϵ and s for the four lithium halides plus LiH.

Before turning to discuss the relation between $k_B T_m$ and the characteristic Coulomb energy E_C , it is of interest to use the Thomas–Fermi variable $Z^{1/3}$ to study regularities in the internuclear separations s of the Li halides (including LiH). Figure 2 shows a plot

TABLE II Measured values of dielectric constants and internuclear separations

	ϵ [refs. noted]	S (Å)	$1/\epsilon s$ (Å) ⁻¹
LiH	12 [2]	2.043	0.041
LiF	9.2 [8] and 9.0 [9]	2.013	0.055
LiCl	11.1 [8] and 11.9 [9]	2.570	0.035
LiBr	12.1 [8] and 13.0 [9]	2.751	0.030
LiI	11.0 [8]	3.006	0.030

FIGURE 2 Nearest-neighbor distance (in Å) versus $Z^{1/3}$.

of s versus $Z^{1/3}$. In terms of this latter independent variable, it is LiF which is anomalous. The other four internuclear separations can be represented by the linear form

$$s = mZ^{1/3} + c \quad (1)$$

where $m = 0.33$ and $c = 1.70$. We also comment here that we studied whether Eq. (1), written for the lithium halides/hydride, would apply for the other four alkali metals Na–Cs replacing Li. The answer is that Eq. (1) continues to work well if the fluorides are omitted, the “constants” m and c in Eq. (1) varying slowly with the nuclear charge of the alkali metal. Since in the Coulomb energy E_C , the product ϵs appears in the denominator, we note that ϵ varies little except for the low value for LiF. However, as noted in [7], discrepancies in ϵ of $\sim 10\%$ are frequently found in the literature. Nevertheless, ϵ for LiF is quite plainly “anomalous” compared with the other four materials in Table II, paralleling the “anomaly” of LiF in the internuclear separation s recorded in the third column. We shall see that these “anomalies” combine to make the comparison of T_m with $1/\epsilon s$ shown in Fig. 3 particularly revealing.

Though the horizontal error bars in Fig. 3 are large because of the errors in the dielectric constant ϵ , it is plain that the possible “anomalous” materials LiF and LiH fit nicely on a linear relation with LiCl, the hydride lying now between the chloride and the fluoride because of the low values of both ϵ and s for LiF recorded in Table II.

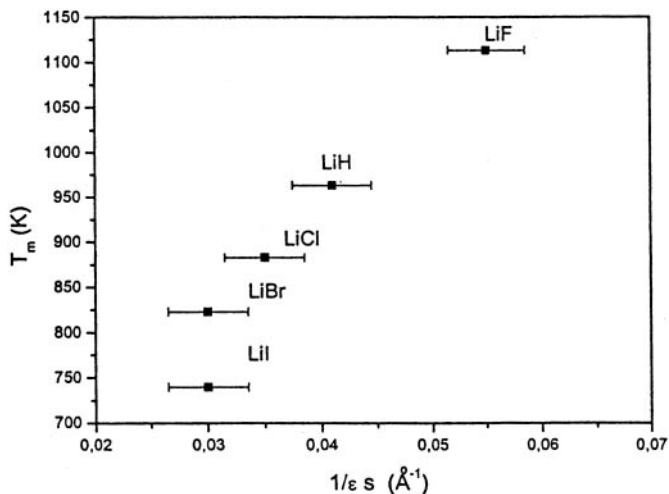


FIGURE 3 Melting points (in K) versus $1/\epsilon_s$ (in \AA^{-1}).

Lithium bromide and iodide are not presently separated by the accuracy of $1/\epsilon_s$, while their melting temperatures differ substantially. It would therefore be of considerable interest if the static (or low-frequency) dielectric constants of these two materials could be remeasured with substantially improved accuracy. Here common expectations concerning the increase in anionic size from Cl^- to Br^- to I^- would suggest that the polarizabilities also increase from Cl^- to Br^- to I^- . Then one expects electron affinities to correspondingly decrease, as is in agreement [10] with experiment, so that also one expects $\epsilon(\text{LiCl}) < \epsilon(\text{LiBr}) < \epsilon(\text{LiI})$ which however is in disagreement with the reported measurements or [8]. Further, data available [8,9] for the Na and K halides displays our expected trend. The disagreement might most likely be due to an erroneously low measured value for $\epsilon(\text{LiI})$, whence it may be noted that a modest increase toward our expectation for $\epsilon(\text{LiI})$ would bring the plot into better form. But even as it stands a reasonable fit of the results in Fig. 3 is given by

$$T_m = (m/\epsilon_s) + C \quad (2)$$

where $m = 1300$ while $C = 405$.

In summary, the first part of the present investigation was motivated from the "characteristic" length for the Thomas-Fermi neutral atom being proportional to $Z^{-1/3}$. The independent variable $Z^{1/3}$, with Z_e now the halogen nuclear charge, then exposed regularities both in the melting temperature T_m and in the internuclear separation s , both Figs. 1 and 2 suggesting that LiF is "anomalous", presumably because of the high electronegativity of F. This "anomalous" behavior of LiF is also reflected in the values of the dielectric constant given in Table II.

Let us conclude by making a few comments in relation to the critical behavior. We have not found critical-point data for the lithium halides/hydride, so we restrict attention to the alkali chlorides NaCl and KCl. From the work of Pitzer [11], preferred values of the critical temperature T_c (due to Kirshenbaum *et al.* [12]) are 3800 K for NaCl and 3470 K for KCl. The critical molar volumes for the ion pairs NaCl and

KCl are $V_c = 420$ and $625 \text{ cm}^3/\text{mol}$, and we find that the product $T_c V_c^{1/3}$ is constant to $\sim 1\%$. For the five alkali metals Chapman and March [13] first noted the constancy of $T_c V_c^\forall$ through this series, with the exponent \forall near 0.3. Subsequently an argument was made [14] for $\forall = 1/3$, and this was confirmed for these metallic fluids by Leys *et al.* [15], where this behavior is argued to be a “fingerprint” of such Coulomb liquids (with alkali-metal ions in a sea of electrons). Leys *et al.* also noted the linearity of a plot of T_m vs. T_c for the five alkali-metal fluids. It is tempting to assume that such linear behavior will hold for the alkali chlorides, and if the available data for NaCl and KCl are used, this then yields

$$T_c = aT_m + b \quad (3)$$

with $a = 13.2$ and $b = 6773 \text{ K}$. But more data on other ionic fluids is needed before such a relationship is reasonably established. If nevertheless this is used, one then predicts a T_c of around 5900 K for LiH, which is at a much higher temperature than its point of decomposition at ordinary pressures.

But nevertheless, the final Fig. 3 shows that T_m correlates well with the Coulomb energy $e^2/\epsilon s$ for the five materials focused on the present study. And the lowest value of the product ϵs for LiF leads to the highest melting temperature $> 1100 \text{ K}$. This leaves LiH placed in Fig. 3 between LiCl and LiF.

Our final comment takes us back to the first sentences of this communication. While we have focused on LiH, we close by recording that LiD, a material of considerable potential for nuclear energy production, has a melting temperature measured as differing by only a few degrees from that of LiH given in Table I. The same dielectric constant $\epsilon \cong 12$ has been indicated [2] for both LiH and LiD.

Acknowledgments

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