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The magnetic susceptibility of crystalline lithium hydride was measured at room temperature (300°A) and at 78°A and was found to be -4.60×10^{-6} per mole with practically no temperature coefficient. One theoretical prediction deviates from the experimental value by 90 percent and another by 130 percent. This discrepancy is interpreted as due mainly to a paramagnetism independent of the temperature which is present in all crystals and which has not been included in the calculations.

THE diamagnetic susceptibility of a mole of atoms or atomic ions may be expressed by

$$\chi = -(Ne^2/6mc^2)\Sigma_i \overline{r_i^2},$$

where χ is the susceptibility per mole, N is Avogadro's number, $\overline{r_i^2}$ is the mean square distance of the i'th electron from the nucleus, the summation extending over all electrons and e, m, c have their usual meanings. Several theoretical methods have been devised for evaluating $\overline{r_i^2}$; one is based on Hartree's method of self-consistent fields,[1] another is due to Van Vleck and Pauling[2] independently, and more recently, Brindley[2] has employed the approximate eigenfunctions of Slater. Angus[2] has also computed $\overline{r_i^2}$ with these eigenfunctions but in greater detail. The diamagnetic susceptibilities derived with these various methods are compared by Angus with the susceptibilities of the alkali halides in solution as measured by Ikenmeyer.[2] The susceptibilities of Pauling are from 10 percent to 60 percent and of Stoner from 50 percent to 80 percent higher than the experimental values. Most of the values of Brindley are also high while those of Angus fluctuate above and below the experimental values by a few percent.

All the theoretical methods deal with electronic systems subject to central forces such as isolated ions in field-free space and since the only data available refer to ions in crystals or in solutions, there is ever present the question of the validity of such comparisons. The chief reassurance has come from the (supposed) additivity of the ionic susceptibilities, suggesting magnetic independence between them, and further there seems as

yet little reason to suspect considerable changes in the mean square radius when a gaseous ion takes its place in a crystal lattice.

In the hope of clarifying some of the uncertainties we measured the magnetic susceptibility of lithium hydride principally because it is the simplest of all ionic lattices.[3] And when its eigenfunction is determined a direct comparison with experiment will be available. It remains to be seen whether the eigenfunction of the crystal will be separable into the eigenfunctions of the ions in the lattice with sufficient accuracy. This separability is implicit in all previous investigations, a matter we shall discuss later. In terms of separate ions, it may be observed that the hydride ion is probably more sensitive than any other to changes in electrical environment. Hence a measurable difference in the susceptibility would probably accompany a change from the gaseous state to the crystalline and the ion might serve to indicate whether all ions undergo such changes.

MATERIALS

We have had the good fortune to obtain crystals of pure lithium hydride. They were furnished by the Maywood Chemical Works, Maywood, N. J., through the courtesy of Dr. H. Osborg. In the light of chemical and magnetic analyses, any ordinary paramagnetic impurity was present in less than 0.002 percent, probably much less, and diamagnetic impurities such as lithium hydroxide, sodium hydride made up less

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[1] Stoner, cited by W. R. Angus, Proc. Roy. Soc. A136, 569 (1932).

[2] Cited by W. R. Angus, see reference 1.

[3] Hylleraas (Zeits. f. Physik 63, 771 (1930)) has confirmed from the heat of sublimation that the lattice is ionic. The crystals are similar to sodium chloride, colorless, hard, melt at a rather high temperature (680°C), all in keeping with an ionic lattice. It was found to be cubic, NaCl type, (Bijvoet and Karssen, Proc. Amst. Acad. 31, 496 (1922)).

than 0.5 percent of the material and could be ignored in magnetic considerations. Chemical analyses for the ferromagnetic impurities, iron and nickel, were made as these more than others were likely to contaminate the material on account of the method of manufacture. The presence of total iron, both free and combined, was found to be less than 7 moles iron in 10 million moles lithium hydride and probably less than 1 in 10 million. No trace of nickel was observed although 1 mole nickel in 5 million lithium hydride would have been detected. It is well known that ferromagnetic metals commonly lose their ferromagnetism when alloyed so that the best sign of ferromagnetic contamination is the magnetic behavior of the substance, the necessary criterion being a dependence of the susceptibility on the field strength. We are unable to observe such a dependence in our materials.

After the lithium hydride had been measured magnetically, it was taken out of the tube for chemical analysis. Different samples gave 99.4 percent, 97.5 percent, 99.5 percent an average of 98.8 percent lithium hydride. The impurities are probably lithium hydroxide and other alkali hydrides. The hydroxide is formed from the hydride and moisture. For this reason the utmost precautions were taken never to expose the hydride to moisture. All the necessary manipulations (such as grinding the crystals to a powder, tamping it into a glass tube for the magnetic measurements) were carried out in a "dry-box" through which dried gases were flowing. In selecting the crystals, any having a blue coloration were avoided. This color is a very sensitive indication of uncombined lithium metal. It is probable that even if some of the faintly blue crystals had been taken no difference would have entered into the magnetic results within our limits of error.

About six months after the first magnetic measurements were taken, we received some lithium hydride from the Maywood Chemical Works which had been made in a more recent lot. Dr. Osborg was good enough to have crystals selected for us which had little likelihood of having touched the metallic walls of the apparatus in which it was made. From these we further selected colorless crystals for the magnetic measurements.

MAGNETIC MEASUREMENTS

The well-known method of Gouy was employed for the magnetic measurements and at low temperatures the method described by Freed.[4] The magnet was of the Weiss type kindly loaned us by Professor W. D. Harkins. It was built with the aid of a grant given to Professor Harkins by the Joseph Henry fund of the National Academy of Sciences. The first two sets of runs listed below were carried out with magnetic fields up to 23,000 gauss and in the remaining runs with fields up to 18,000 gauss.

The magnetic susceptibility was also determined at 78°A to enhance the effect of any paramagnetic impurity since paramagnetic susceptibility usually varies almost inversely as the absolute temperature. That is, the paramagnetic impurity would have its room temperature susceptibility almost quadrupled at 78°A.

As has been noted, we were unable to detect any variation in the susceptibility with field strength such as one would expect from the presence of any ferromagnetic impurity.

On May 21, 1934, the magnetic susceptibility per mole of lithium hydride was determined at room temperature (300°A) as -4.42×10^{-6}.

On May 22, 1934, another sample of the same crystals was taken and independent magnetic measurements at room temperature (300°A) gave -4.68×10^{-6} per mole. The deviations from the average of these two sets of runs is 3 percent, a little high, perhaps because of the irregularities in the packing of the powder in the tubes.

On December 10, 1934, lithium hydride which had been prepared afresh by the Maywood Chemical Works was measured under conditions which were very different from those which had prevailed in the other measurements. The glass tube containing the powder was changed, the pole gap of the magnet and hence range of magnetic fields were different. The susceptibility per mole was found in a series of runs as -4.65×10^{-6} in satisfactory agreement with the values obtained six months previously. These crystals had been measured in a Dewar vessel at room temperature. The temperature was then lowered to 78°A (the temperature of liquid nitrogen) and the susceptibility at this temperature was -4.60

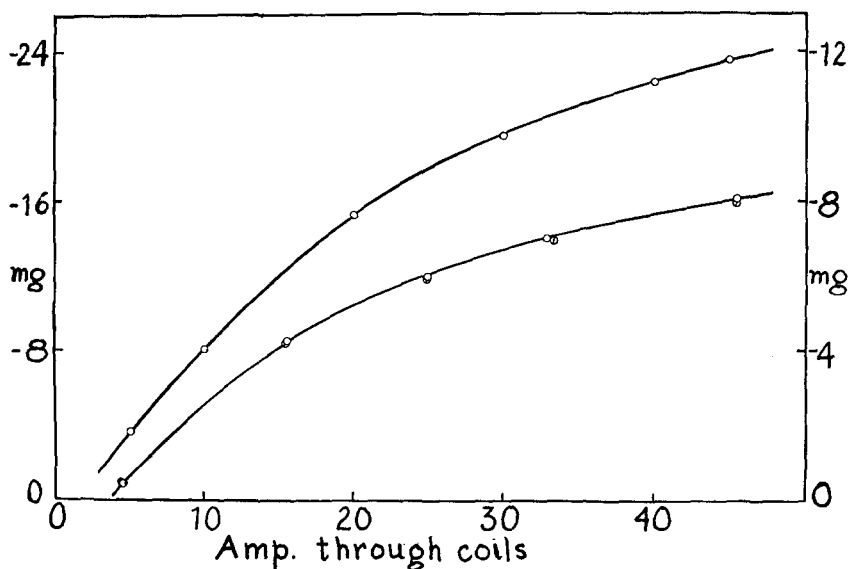[4] S. Freed, J. Am. Chem. Soc. 52, 2702 (1930).

FIG. 1. Change in apparent weight in magnetic field. Water for calibration: upper curve, weight at left. Lithium hydride: lower curve, weight at right. Clear circles at room temperature 300°A. Halved circles at 78°A.

$\times 10^{-6}$, an increase of 1.1 percent. This difference is real as the experimental method is especially suitable for measuring differences resulting from changes in temperature. At room temperature, the percentage of the susceptibility which may be ascribed to a paramagnetic impurity is about $(78/222) \times 1.1 = 0.35$ percent. The deviations between measurements within a set of runs occurred in the third decimal place.

The figure gives the curves obtained from the measurements both of water, which served for calibration, and of lithium hydride at 300°A and at 78°A.

We conclude, then, that the molal susceptibility of lithium hydride in the crystalline state is -4.60×10^{-6} within about 2 percent.

DISCUSSION OF RESULTS

The molal susceptibility of lithium hydride predicted by Pauling is -8.65×10^{-6} and by both Brindley and Angus -10.54×10^{-6} and the experimental value is -4.60×10^{-6}, truly another order of magnitude. We are faced with several possibilities of which the more important are: (1) The mean square radii of the electrons in the

ions (hydride ion, especially) have undergone a shrinkage of 50 percent or more; (2) a factor which does not operate in isolated ions introduces in crystals a paramagnetism which is practically independent of the temperature. On this basis the measured diamagnetic susceptibility cannot be related exclusively to the term of the mean square radii. This factor, we are inclined to believe, accounts for most of the discrepancy.[5]
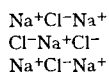
[5] That there may also be a possible shrinkage in the $\overline{r_i^2}$ of the electrons is suggested by the fact that the radius of the hydride ion as defined for x-ray data is less in lithium hydride than in other alkali hydrides. Zintl and Harder (Zeits. f. physik. Chemie **B14**, 265 (1931)) give the following lattice distances for the alkali hydrides. Upon subtracting the radii of the positive ions as given by Zachariasen (Zeits. f. Krist. **80**, 137 (1931)) from one-half the lattice distance, the radii of the hydride ions are obtained. These are listed in the last column.

|	Lattice distance	r_{M^+}	r_{H^-}
LiH	4.084	0.68	1.36
NaH	4.880	0.98	1.46
KH	5.700	1.33	1.52
RbH	6.037	1.48	1.54
CsH	6.376	1.67	1.52

It need not follow that there is any difference in the $\overline{r_i^2}$ of the electrons in the various hydride ions. Even if the effect on the $\overline{r_i^2}$ were as large as is here suggested, it would be small compared with the discrepancy between the computed and experimental susceptibilities and we are inclined to the view that the ignored possibility (2) is a dominant factor.

Van Vleck[6] has shown that in atomic systems having spherical symmetry, the instantaneous angular momentum of the $^1S_0$ state is zero as well as its average angular momentum. In polyatomic systems, among which we may include crystals, the instantaneous angular momentum is not zero, even when the stationary state is $^1\Sigma_0$ that is, even when the average angular momentum is zero. The perturbation theory foresees a paramagnetic contribution from the square of these instantaneous fluctuations in angular momentum which of necessity is positive. If the frequency differences between the various states is high as compared with kT this paramagnetism would be independent of the temperature. The magnitude of this "fluctuation" paramagnetism which we shall call the "Van Vleck paramagnetism" is in many instances great enough to account for the discrepancy between the experimental susceptibility and the various computed values. As examples we may cite the magnetic measurements[7] on $KMnO_4$, $K_2Cr_2O_7$, K_2MoO_4 and UO_2SO_4 which were selected to show this effect in MnO_4^-, $Cr_2O_7^-$, MoO_4^- and UO_2^{++}. In these instances the paramagnetism was more than great enough to overbalance the total diamagnetism of the crystal and yet it was small compared with the usual paramagnetism which varies with the temperature.

There is no doubt that the alkali halides may undergo quantum transitions[8] to states associated with angular momentum. The same is doubtless true in lithium hydride[9] also. If we symbolize the NaCl lattice as

$$Na^+Cl^-Na^+$$
$$Cl^-Na^+Cl^-$$
$$Na^+Cl^-Na^+$$

upon absorbing ultraviolet light, the crystal is activated into a state thus,

$$Na^+Cl^-Na^+$$
$$Cl^-Na^0Cl^0$$
$$Na^+Cl^-Na^+$$
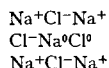
to which the blue color has been ascribed.[8] Other transitions are possible also.

The final state we have been discussing is paramagnetic but it is not the number in the final state we are concerned with. It is rather the fluctuation from the basic state to the activated state which accounts for the paramagnetism independent of the temperature. The conclusion is then that some of the diamagnetism originating in the mean square radii is masked by the Van Vleck paramagnetism in all ionic crystals as well as in others; and that it is erroneous to employ experimental diamagnetic susceptibilities alone to furnish average radii of ions or to serve as criteria for the accuracy of such approximate eigenfunctions as have been proposed. In some instances, it is true such errors may not be great, a matter which requires separate investigation. Theories which furnish correct mean square radii would yield greater diamagnetic susceptibilities than are to be found experimentally and hence the values of Pauling or of Stoner should not be rejected because of "poor agreement" with the experimental susceptibilities.

From this point of view, we would expect the additivity of ionic susceptibilities not to hold except as a rough approximation especially among dissimilar compounds. One would expect some difference between the diamagnetism of crystals and of their solutions and possibly also, but to a much lesser degree, some departure from linearity in the susceptibility as a function of the concentration in regions of high concentration.

Very opportunely, Hoare[10] has remeasured with considerable care the diamagnetic susceptibilities of salts with rare gas ions and we shall quote some of his conclusions:

It will be seen then that no conclusive evidence as to the validity of the additivity principle can be derived from this table, especially from Ikenmeyer's results; the results of the present investigation indicate, however, that it may be true to a first approximation.

Hocart measured the susceptibilities of the chlorides in the crystalline form and in aqueous solution, finding the results in the former state to be less than the latter. It would appear, therefore, from the results for the bromides and iodides, that the result found by Hocart for two salts might very well be in agreement with a general principle.

This conclusion is strengthened by Kido's results.

[6] J. H. Van Vleck, *Electric and Magnetic Susceptibilities*, Oxford University Press, 1932.
[7] S. Freed and C. Kasper, J. Am. Chem. Soc. **52**, 4671 (1930).
[8] R. Hilsch and R. W. Pohl, Zeits. f. Physik **68**, 721 (1931).
[9] F. Bach and R. F. Bonhoeffer, Naturwiss. **20**, 940 (1932).

[10] F. E. Hoare, Proc. Roy. Soc. **A147**, 88 (1934).