

**Corresponding Member of
the USSR Academy of
Sciences V. M.
VDOVENKO, Ya. V.
VASIL' EV,**

Yu. V. DUBASOV

1964

SovietRxiv

Abstract

Full Text

PHYSICS

Corresponding Member of the USSR Academy of Sciences V. M. VDOVENKO,
Ya. V. VASIL' EV,
Yu. V. DUBASOV

MAGNETIC SUSCEPTIBILITY OF RADIUM CHLORIDE AND BROMIDE

A magnetochemical study of radium compounds is of substantial interest, since the data obtained may be used to study the structure and nature of the chemical bond in these compounds. Interest in such a study is also explained by the fact that, according to the data of the only work on the magnetochemistry of radium, by Kuri and Shenevo⁽¹⁾, radium chloride is weakly paramagnetic. The specific susceptibility of RaCl_2 is equal to $\chi_g = +1.05 \cdot 10^{-6}$, and the molar susceptibility $\chi_{mol} = +312 \cdot 10^{-6}$. Since the cited work was carried out by classics of magnetochemistry, the result they obtained aroused no doubts and is cited in the chemical literature^(2,3) without any explanation.

Taking into account, however, that radium (all electron shells are closed, term 1S_0) does not belong to the transition elements, whose compounds are characterized by polarization (Van Vleck) paramagnetism χ_p , considerably exceeding the precessional diamagnetism χ_d ⁽⁴⁾, one may suppose that the paramagnetism of RaCl_2 observed in⁽¹⁾ was due to impurities of strongly magnetic substances. The nature of these impurities could be as follows: mechanical contamination of the preparation by ferromagnetic or paramagnetic substances, or color centers appearing as a result of the interaction of the radioactive radiations of radium and its decay products with the substance. Thus, the result obtained in⁽¹⁾ has no satisfactory explanation. It is either a consequence of experimental error or a consequence of radiation disturbances of the crystal lattice caused by the radioactivity of radium.

The present work is devoted to measuring the magnetic susceptibility of radium chloride and bromide. The RaBr_2 sample measured in preliminary experiments proved to contain ferromagnetic impurities. Nevertheless, the specific susceptibility of this preparation, extrapolated to $H = \infty$, was $-(0.23 \pm 0.1) \cdot 10^{-6}$ and indicated that radium bromide is diamagnetic. After this, measurements were undertaken on purer samples. The salts were prepared by the usual method⁽⁵⁾, but with measures taken to prevent contamination by ferromagnetic impurities. The preparations contained about 0.2% of other alkaline-earth elements⁽⁶⁾. The anhydrous salts RaCl_2 and RaBr_2 were sealed in ampoules of glass 29, with an outside diameter of 5 mm and a wall thickness of about 0.1 mm.

A RaBr_2 sample weighing 0.070 g and a RaCl_2 sample weighing 0.049 g were measured approximately 4 days after sealing.*

To reduce the measurement error, a temperature regime was selected in which the susceptibility of the empty ampoule was equal to zero. This regime corresponded to a temperature of -1° . Susceptibility measurements were carried out by the Faraday method in an atmosphere of dry nitrogen at -1° and 100° , and in magnetic fields of various strengths: 18600, 16900, 14800, and 10900 oersteds. To measure the forces acting on the ampoule with the substance in the magnetic field, quartz torsion microbalances with a sensitivity of about $0.5 \cdot 10^{-6}$ g were used. Equilibrium of the balances was achieved by the force arising from the interaction of a permanent magnet,

* Radiometric measurements showed that the ampoules contained 0.070 g of RaBr_2 and 0.049 g of RaCl_2 . The error of these measurements was about 5%.

mounted on the balance beam, with a solenoid. The balancing process was carried out automatically by means of a photocompensation circuit. After the measurements, the ampoule with RaBr_2 was opened and its susceptibility was checked under conditions corresponding to the conditions used for measuring the samples. No appreciable deviations of the susceptibility of this ampoule from χ_Γ of the empty ampoules used for calibration were found. As the standard, chemically pure KCl, recrystallized three times and calcined at 500° , was used. Potassium chloride was sealed in ampoules made from the same tube as the sample ampoules. The ampoules with the standard did not differ in size or shape from the sample ampoules. The magnetic susceptibility of the standard was taken as $\chi_{mol}^{\text{KCl}} = -38.7 \cdot 10^{-6}$ (7). The error in determining the absolute values of χ was approximately 4%.

The measurements showed that the preparations contained ferromagnetic impurities in extremely small amounts. Therefore the specific magnetic susceptibility of radium chloride depended only weakly on the field strength and was extrapolated to $H = \infty$, so that the value $\chi_\Gamma^{\text{RaCl}_2} = -0.31 \cdot 10^{-6}$ should be regarded as sufficiently reliable. The susceptibility of radium bromide, however, was practically independent of the field H and was equal to $\chi_\Gamma^{\text{RaBr}_2} = -0.29 \cdot 10^{-6}$. Thus, as was to be expected, the radium compounds studied proved to be diamagnetic, in contrast to the result obtained in (1); moreover, the susceptibility of the compounds studied is practically independent of temperature. The molar susceptibilities of RaCl_2 and RaBr_2 are $-(92 \pm 4) \cdot 10^{-6}$ and $-(112 \pm 4) \cdot 10^{-6}$, respectively.

The data obtained by us give grounds to suppose that the radium chloride sample used for the measurements in work (1) contained ferromagnetic impurities, which in weak magnetic fields made a substantial contribution to the susceptibility. The work does not indicate whether the susceptibility of RaCl_2 depends on the field strength and on temperature. If Curie and Chéneveau measured the susceptibility of RaCl_2 at one value of the field strength, it is quite probable that they could not establish the contamination of the preparation, which led

them to an erroneous result.

Thus, the experimentally established fact of the diamagnetism of RaCl_2 and RaBr_2 indicates that, in magnetochemical respect, radium does not differ from barium, as was thought earlier (3), and that the difference between them consists only in the magnitude of the magnetic susceptibility, i.e., apparently, it does not depend on the radioactivity of radium but is determined by the difference in the number of electrons of the atoms indicated.

As is known (8), the experimentally determined susceptibility of a weakly magnetic substance χ is equal to the sum of the diamagnetic χ_d and paramagnetic χ_p components. The value χ_p is a structurally sensitive quantity and therefore makes it possible to estimate the deformation of the electron shells of the atoms of a compound. The presence of χ_p in an ionic compound indicates the appearance of a covalent bond between ions (7). Therefore, determination of the magnitude of the paramagnetic component χ_p of the compounds RaCl_2 and RaBr_2 is of definite interest.

According to Dorfman (7), to calculate χ_p the diamagnetic susceptibility χ_d of the compound must be known; χ_d is determined from the Kirkwood relation

$$\chi_d = -\frac{NA^2e^2a_0^{1/2}}{4mc^2}\sqrt{k\alpha_\infty}. \quad (1)$$

In this relation α_∞ is the polarizability of the compound for light of wavelength $\lambda = \infty$; a_0 is the Bohr radius; k is the number of electrons in the compound; the remaining designations are conventional (9). Since experimental data on the polarizability of crystalline RaCl_2 and RaBr_2 are lacking, we calculated these quantities from the assumption of additivity of ionic polarizabilities. The initial data used were

the polarizability of the radium ion was taken as $\alpha_\infty^{\text{Ra}^{2+}} = 2.3 \text{ \AA}^3$ (5), and the ionic polarizabilities for the crystalline state as $\alpha_\infty^{\text{Cl}^-} = 3.30 \text{ \AA}^3$ and $\alpha_\infty^{\text{Br}^-} = 4.47 \text{ \AA}^3$ (10). The calculated values are $\alpha_\infty^{\text{RaCl}_2} = 8.9 \text{ \AA}^3$ and $\alpha_\infty^{\text{RaBr}_2} = 11.3 \text{ \AA}^3$. The results of calculating the diamagnetic and paramagnetic components for radium chloride and bromide are given in Table 1. The corresponding values for barium chloride, taken from (7), are also given there.

Table 1

Polarizabilities, diamagnetic and paramagnetic susceptibilities of BaCl_2 , RaCl_2 , and RaBr_2

Compound	$\alpha_\infty, \text{ \AA}^3$	$-\chi_d \cdot 10^6, \text{ calc.}$	$-\chi \cdot 10^6, \text{ exp.}$	$\chi_p \cdot 10^6$
BaCl_2	8.5	85.5	72.6	12.9
RaCl_2	8.9	103	92	11
RaBr_2	11.3	132	112	20

It is clear from the table that the values of χ_p for BaCl_2 and RaCl_2 are close (allowing for the error in calculating χ_p). Apparently, in the radium compounds studied, as in the analogous barium compounds, the chemical bond is predominantly ionic in character, and, in addition, a covalent bond appears between the ions.

The ionic susceptibility of radium, which is of interest both from the magnetochemical standpoint and for the study of the electron distribution in Ra^{2+} , can be calculated under the assumption of additivity of ionic susceptibilities. According to ⁽¹¹⁾, the susceptibilities of Cl^- and Br^- are: $\chi^{\text{Cl}^-} = -22.9 \cdot 10^{-6}$ and $\chi^{\text{Br}^-} = -33.4 \cdot 10^{-6}$. The susceptibility of the Ra^{2+} ion is equal to $-46 \cdot 10^{-6}$ and is in satisfactory agreement with the value $\chi^{\text{Ra}^{2+}} = -43.7 \cdot 10^{-6}$, obtained by substituting the experimental value of the ionic polarizability $\alpha_{\infty}^{\text{Ra}^{2+}} = 2.3 \text{ \AA}^3$ ⁽⁵⁾ into relation (1).

The authors express their deep gratitude to Prof. S. M. Ariya for providing the opportunity to carry out this work.

Received
7 VII 1964

REFERENCES

1. P. Curie, C. Cheénveau, *J. Phys.*, **2**, 796 (1903).
2. *Nouveau Traité de Chimie Minérale*, **4**, Paris, 1958.
3. K. Bagnall, *Chemistry of the Rare Radioactive Elements*, IL, 1960.
4. Ya. G. Dorfman, *Magnetic Properties and Structure of Matter*, Moscow, 1955.
5. V. M. Vdovenko, Yu. V. Dubasov, *Radiokhimiya*, **7**, No. 1 (1965).
6. G. V. Gorshkov, Z. G. Gritchenko et al., *Atomic Energy*, **7**, 5, 445 (1959).
7. Ya. G. Dorfman, *Diamagnetism and the Chemical Bond*, Moscow, 1961.
8. J. H. Van-Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford, 1932.
9. J. C. Kirkwood, *Phys. Zs.*, **33**, 2, 57 (1932).
10. G. B. Bokii, S. S. Batsanov, *Bulletin of Moscow University*, No. 2, 147 (1952).
11. F. E. Hoare, G. W. Brindley, *Proc. Phys. Soc.*, **49**, 275, 619 (1937).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.