Variation of the Magnetic Properties of Barium with Temperature

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A discontinuity in the resistivity-temperature curve for pure barium at about 370°C has led to the suggestion that two modifications of the crystal structure (α and β-barium) exist, below and above this temperature respectively. Further, the similarity of the curve to that for the ferromagnetics makes it reasonable to suppose that a discontinuity in the susceptibility-temperature curve (i.e., a Curie point) may exist. The susceptibility has been measured over a range of 400°C and such a discontinuity is found to exist at about 350°C. The experimental results are completely at variance with the current theory for paramagnetics.

INTRODUCTION

IN a recent paper, Rinck[1] reports the variation of the electrical resistivity of pure barium as a function of the temperature, and finds a sharp discontinuity in the slope of this curve at about 370°C. On the basis of this measurement he supposes two types of structure, α and β-barium, to exist, below and above this temperature, respectively. The resistance-temperature curve bears a strong resemblance to that for the ferromagnetics and it would therefore appear possible that a discontinuity in the magnetization-temperature curve should occur, similar to that occurring at the Curie point in the ferromagnetics. As no previous measurements for the susceptibility of barium above room temperature exist, this possibility has here been investigated.

PREPARATION OF THE METAL

The barium metal was obtained from Messrs. Eimer and Amend, New York, and designated by them as "C.P." For the purposes of measurement the specimens had to be in the form of small cylinders about 2 cm long and 0.3 cm in diameter. Because of the fact that barium oxidizes rapidly on exposure to the air, even at room temperature, the specimens had to be protected at all times. For the temperature measurement the specimens were prepared as follows.

The metal was melted into a small quartz tube under high vacuum, during which process the surface of the metal was covered with a hard shell due to chemical reaction with the quartz. The quartz tube was then broken off and the foreign surface matter ground off with a small carborundum wheel under ligroine. The metal cylinder was then introduced into a second, very thin-walled, quartz tube and evacuated. It was found the metal specimens so produced had a very dull appearance, quite unmetallic looking. It was apparent that the ligroine used to protect the specimens before evacuation had attacked the metallic surface. To remedy this the following artifice was used. Pure argon gas (at *ca.* 1 mm pressure) was introduced into the tube, and the latter made several times longer than the metal cylinder and of such a diameter that the barium specimen could slide inside it. The end of the tube containing the metal was now placed in an electric furnace and held at a temperature of about 500°C for some minutes. It was found that the metal apparently slowly evaporated depositing the surface contamination on the walls of the quartz, in the immediate vicinity of the metal. The barium was now slid to the other end of the tube and the quartz sealed off as near the specimen as possible. This final specimen was silvery in appearance, and provided the temperature was not raised much above 400°C no evidence of further evaporation or chemical change could be detected. At no stage in the process was iron allowed to come in contact with the metal. Earlier attempts at preparation of suitable specimens without all these precautions gave erratic values of susceptibility.

[1] E. Rinck, Comptes Rendus **193**, 1328–1330 (1931).

METHOD OF MEASUREMENT

The Weiss translation method with permanent magnet dynamometer in the form described by Foex and Forrer[2] was adopted. Only slight modifications were introduced, notably the use of Balsa wood for the beam and the sensitive mirror system described previously by Montgomery.[3] The apparatus was set up in a constant temperature room and all observations made through a window outside this room. Temperatures were recorded by means of a chromel-alumel thermocouple which was calibrated against a standard platinum, platinum-rhodium couple.

The holder for the specimen for the measurement at room temperature consisted of a quartz tube, very nearly the same size as the metal, sealed at one end and having a small amber plug at the other. The specimen was wetted with ligroine and quickly introduced into the holder, the thin surface film of ligroine protected the metal from oxidation and was so thin that its magnetic properties were negligible. The susceptibility was measured in terms of distilled water ($\chi = -0.72 \times 10^{-6}$) and gold ($\chi = -0.145 \times 10^{-6}$) the values agreeing within one percent. Corrections for the susceptibility of the air were applied, the product of mass susceptibility and density being taken as $+0.029 \times 10^{-6}$. In the temperature measurement no correction was necessary for the quartz container as the susceptibility of quartz is independent of temperature.[2] Finally the susceptibility was measured at various field strengths over a range of about five kilogauss as a test on the presence of any ferromagnetic impurity.

RESULTS

In Table I are given the results for the susceptibility of barium at various temperatures and these values are plotted in Fig. 1. It will be seen that a very definite discontinuity in the temperature-magnetization curve occurs at about 350°C which, allowing for specimen differences, agrees well with Rinck's estimate. Beyond this point the susceptibility is somewhat smaller as was predicted. Each point on the curve is the

TABLE I. *Variation of susceptibility with temperature.*

Temperature	Mass suscept.	Temperature	Mass suscept.
20°C	$+0.147 \times 10^{-6}$	312°C	$+0.332 \times 10^{-6}$
76	0.162	326	0.345
110	0.172	336	0.356
145	0.188	343	0.358
185	0.212	350	0.359
224	0.234	360	0.372
246	0.258	372	0.383
270	0.280	384	0.396
288	0.298	393	0.406
300	0.316	400	0.415

mean of at least three and usually of more than three determinations. The values were found to be perfectly reproducible, that is to say it was found to be immaterial whether one started at 20°C and went up or started at 400°C and came down. The possibility of chemical change was thus excluded.

It is pertinent to inquire whether the effect might not be due to a ferromagnetic impurity having its Curie point in the vicinity of 350°C.[4] That this is not the case may be seen from Table II. In the fourth column, under the heading "mass susceptibility estimated," are given the calculated values of the susceptibility on the assumption that the change in the vicinity of 350°C is entirely due to ferromagnetic impurity.
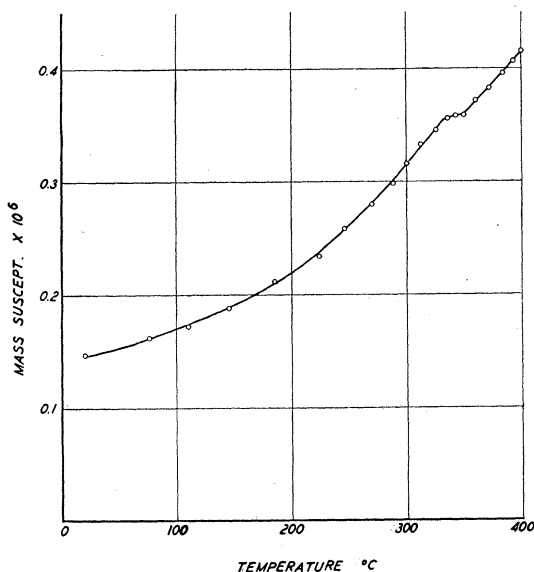

FIG. 1. Mass susceptibility of barium as a function of temperature.

[2] G. Foex, R. Forrer, J. de Physique [6] 7, 180–187 (1926).

[3] C. G. Montgomery, Phys. Rev. [2] 36, 498–505 (1930).

[4] The Curie point of pure nickel is about 359°C.

TABLE II. *Variation of susceptibility with field (H) at 20°C.*

Magnet current (amp.)	H	Mass susceptibility observed	Mass susceptibility estimated
2.5	3300	+0.153×10⁻⁶	0.171
3.0	3960	0.152	
3.5	4570	0.150	
4.0	5080	0.146	
5.0	5840	0.145	
6.0	6300	0.148	
7.0	6700	0.146	
8.0	7000	0.147	
9.0	7300	0.147	0.147
14.0	8150	0.150	0.145

By extrapolating the part of the temperature curve below about 335°C it is evident that the change in susceptibility amounts to at least $\Delta\chi = 0.02\times10^{-6}$ and is probably more. Knowing the field strength at which the temperature measurements are made (7300 gauss) we may thus calculate σ in the Honda relation $\chi_{obs.} = \chi_\infty + \sigma/H$ and hence estimate the susceptibility at various field strengths.

By extrapolating the observed values to infinite field we find $\chi = +0.145\times10^{-6}$, or in other words the actual value of σ is 29.5, while the value which would be necessary to cause the effect observed, if due to ferromagnetic impurity, is 146, say five times as great. Hence even in the unlikely event that all the ferromagnetic im-

purities present have Curie points in the vicinity of 350°C, their amount is in nowise sufficient to cause the observed change.

These measurements were all carried out on two specimens with good agreement. The accuracy of the determination of the susceptibility at room temperature is about one percent, that of the relative temperature measurements being slightly better.

The present theory of paramagnetism is quite unable to account for the results observed here, namely an increase in the paramagnetic susceptibility with increasing temperature. If we choose to regard the phenomenon as due to a decrease of a diamagnetic component, the behavior is still anomalous since diamagnetism is a property which should be, theoretically, independent of temperature. Until allowance for the effect exchange phenomena have on magnetic properties is made we can hardly hope for a satsfactory explanation of the known magnetic properties of metals.