STUDY OF ELECTRON PARAMAGNETIC RESONANCE IN GLASSES CONTAINING TWO TRANSITION ELEMENTS

PHYSICS

1969

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

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UDC 538.113

PHYSICS

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STUDY OF ELECTRON PARAMAGNETIC RESONANCE IN GLASSES CONTAINING TWO TRANSITION ELEMENTS

MANIFESTATION OF CROSS-RELAXATION AND SPIN-DIFFUSION PROCESSES IN CERTAIN COBALT-CONTAINING GLASSES

(Presented by Academician L. A. Artsimovich, 22 VII 1968)

In work ([1]) it was noted that the introduction of Co into oxide glasses containing copper leads to a weakening of the e.p.r. signal of Cu^{2+} at nitrogen temperatures in comparison with the Cu^{2+} signals in the corresponding cobalt-free

Fig. 1. Dependence of the intensity of the e.p.r. signal of certain paramagnetic ions in oxide glasses on the concentration of these ions and on the Co content. **A** –dependence of the intensity of the e.p.r. signal of Cu^{2+} in a borate cobalt-containing glass on the Co content at a constant copper concentration (2 cat.%): a –experiment, b –$1-an$, c –kn^{-2}, d –$bn^{-4/3}$. **B** –dependence of I/I_0 for VO^{2+} (a –borate glasses, b –silicate, c –phosphate), Cu^{2+} (d), Mn^{2+} (e) and W^{5+} (f) on the concentration of these ions in the glass N at a constant Co content (2 cat.%)

glasses, and the degree of this weakening depends both on the concentration of Cu^{2+} in the initial glass and on the content of the cobalt introduced.

In the present work, the investigation of the influence of Co on the e.p.r. spectra of Cu^{2+} has been continued, and an attempt has also been made to study the influence of Co on the spectra of several other ions (VO^{2+}, Mn^{2+}, and W^{5+}) in oxide glasses. The measurements were carried out on an RE 1301 radiospectrometer at nitrogen temperatures. The concentrations of paramagnetic ions were estimated with the aid of a standard sample, $CuCl_2 \cdot 2H_2O$. The results of the measurements are presented in Figs. 1 and 2.

Figure 2

Figure 2: Figure 2

Discussion of Results

1. The results presented show that, in various glass-forming matrices (borate, silicate, and phosphate glasses), the introduction of Co even in comparatively small amounts (~ 0.5 cat. %) leads to a considerable weakening of the EPR signal of ions II (where II = Cu^{2+}, VO^{2+}, Mn^{2+}, and W^{5+}), if the concentration of these ions exceeds a certain value that depends on the nature of the ions and on the Co content.

The identical effect of Co on the EPR spectra of paramagnetic ions with such different electronic configurations in glasses that have different oxidation–reduction potentials and differ in their structure indicates the identical nature of this effect for all the glasses studied, which cannot be reduced to a simple shift of the equilibrium to the right.

Paramagnetic ion + $Co^{2+} \leftrightarrow$ diamagnetic ion + Co^{m+}

It remains to relate the nature of this effect to the specific feature of the Co^{2+} ion that is inherent in it in all oxide glasses, namely: Co^{2+} in the oxygen octahedron of an oxide glass has very short spin-lattice relaxation times, which preclude observation of EPR at liquid-nitrogen and higher temperatures. The paramagnetic ions studied (VO^{2+}, Cu^{2+}, Mn^{2+}, and W^{5+}), on the contrary, have long spin-lattice relaxation times.

Fig. 2. EPR spectra of VO^{2+}, W^{5+}, Mn^{2+}, and Cu^{2+} at liquid-nitrogen temperature and the Co^{2+} EPR spectrum at helium temperature, typical for oxide glasses in the concentration range studied (the horizontal sweep scale is preserved)

2. Thus, glasses containing two types of paramagnetic ions, II and Co^{2+}, may be regarded as two spin systems, one of which (Co^{2+}) is characterized by very short spin-lattice relaxation times, while the other (II) by sufficiently long ones; this leads to the appearance of a difference in the spin temperatures of these systems. In the presence of thermal contact between these systems, realized through a system of dipole–dipole interactions, equalization of their temperatures (cross-relaxation) is possible.

Cross-relaxation processes, as is known, imply transitions between nearly equidistant or multiple equidistant levels of two spin systems. In the materials we studied, the EPR lines are inhomogeneously broadened, since they constitute the envelope of all possible lines of anisotropic hyperfine spectra of Cu^{2+}, VO^{2+}, Mn^{2+}, Co^{2+}, and W^{5+}. It follows from Fig. 2 that there is some region of overlap between the spectra of Co^{2+} and each of the ions Cu^{2+}, VO^{2+}, and Mn^{2+}. These overlap regions indicate the presence of equidistant levels in the

Co^{2+} and II systems and, consequently, two-spin cross-relaxation processes are possible for the ions corresponding to them.

3. However, as is evident from Fig. 2, the overlap regions of the spectra of Co^{2+} and II (for example, Cu^{2+} or VO^{2+}) are small, i.e., the number of II ions that

can relax as a result of two-spin cross-transitions, is small (in the case of VO^{2+}, for example, no more than 3-5% of the total number of ions contributing to the EPR signal). Nevertheless, as is seen from Fig. 1B, at sufficiently high concentrations of VO^{2+} the intensity of the EPR signal is equal to zero, i.e., there occurs a sharp decrease in the spin-lattice relaxation time for all VO^{2+} ions, irrespective of the part of the spectrum to which they contribute. It may therefore be assumed that relaxation of the main part of spins P occurs by spin diffusion within the inhomogeneously broadened EPR line, caused by the spin-temperature gradient produced in spin systems P as a result of cross-relaxation of part of the spins.

Thus, if the magnetization of the spin system P at the time t at the point r is equal to $M(r,t)$, then

$$\partial M/\partial t = (\partial M/\partial t)_{\text{c.r.}} + (\partial M/\partial t)_{\text{diff}}, \tag{1}$$

where the first term expresses the rate of change of the magnetization as a result of cross-relaxation between P and Co^{2+}, and the second is the rate of change of the magnetization as a result of spin diffusion.

4. The intensity of the EPR signal of P ions in a cobalt-containing glass can be expressed as $I = I_0(1-f)$, where I_0 is the signal intensity of P ions in the initial cobalt-free glass; f is the probability that a P ion has relaxed through Co^{2+} ions. From the arguments given above and from equation (1) it follows that f will be determined by the probability of cross-relaxation between P and Co^{2+} and by the rate of spin diffusion in system P.

5. Analysis of the results shown in Fig. 1B and representing the dependence of $1-f$ on the concentration of P ions in the corresponding cobalt-free glass makes it possible to draw the following conclusions:

a) The very character of the dependence (a decrease in the intensity of the P signal with increasing P concentration at constant Co content) indicates that it cannot be caused by chemical exchange between Co^{2+} and P.

b) It has been established that the number of P ions that can relax as a result of cross-relaxation, in the investigated range of P concentrations, is approximately proportional to the P content. Consequently, the quantity I/I_0 should practically not change at different concentrations of P and, in the case of VO^{2+}, for example, should not be less than 0.95, which is in fact observed at VO^{2+} concentrations below $\sim 10^{19}$ g^{-1} (region I in Fig. 1B). In this concentration region the rates of spin diffusion are small.

In region III, where the concentration of VO^{2+} is $> 5 \cdot 10^{20}$ g^{-1}, the rate of spin diffusion exceeds the rate of cross-relaxation of the individual spin packets contributing to the inhomogeneously broadened EPR line, and such a line, in accordance with the theory of Brombergen et al. ([2]), should relax as a whole, i.e., the EPR signal of VO^{2+} should be absent, which is indeed observed ($I/I_0 = 0$).

c) At the present stage we did not set ourselves the goal of clarifying the character of the relative efficiency of the processes of cross-relaxation and spin diffusion as a function of the nature of ion P. However, it follows from Fig. 1B that such a dependence exists. Thus, for example, for VO^{2+} and Cu^{2+} the dependence of $1 - f$ on the concentration of these ions is approximately the same, while for Mn^{2+} and W^{5+} it is apparently weaker. As for W^{5+}, as follows from Fig. 2, the EPR lines of W^{5+} and Co^{2+} do not overlap. Therefore the mechanism of cross-relaxation between W^{5+} and Co^{2+} must be more complicated than for the other ions studied.

6. Figure 1A shows the dependence of the intensity of the EPR signal of Cu^{2+} on the content of Co^{2+} in borate glass of composition: $60BO_{1.5} + 2CuO + m\,BaO + n\,CoO$, where $m + n = 38$, $n = 1, 2, 3, 4, 5, 10, 15$ and 18 cat.%. The amount of Cu^{2+} in the initial glass is $\sim 1.5 \cdot 10^{20}$ g^{-1}, and Co is present in glasses melted in a neutral atmosphere in the form of Co^{2+} (the dependence presented is a function of the Co content in the batch composition).

It follows from Fig. 1A, in which, in addition to the experimental curve, the theoretical dependences are presented, that at comparatively low Co concentrations the function $f = an$ (where $a = 0.255$).

For the study of the relaxation processes of P ions through Co^{2+}, in principle some propositions of the theory of nuclear relaxation through paramagnetic centers are applicable. Equation (1) is applicable to both processes; moreover, the diffusion term for the change in the magnetization of the nuclear and electronic spin systems leads to analogous results. In particular, the theory of nuclear relaxation through paramagnetic centers [3] gives, for the regions of fast and limited diffusion, a dependence of the relaxation probability f that is linear with respect to n, which is what is observed in our case for $n < 3$. The first term of equation (1), in the case of nuclear relaxation through paramagnetic centers, expresses the rate of change of the magnetization of the nuclear spin system as a result of direct interaction with paramagnetic centers. The different nature of the processes described by the first term of equation (1) for nuclear relaxation and for the relaxation considered by us leads to a different dependence of the relaxation rate on n. In our case, at large n the dependence $f(n)$ takes the form $f = 1 - bn^{-4/3}$ for $3 < n < 5$ and $f = 1 - kn^{-2}$ for $n > 10$.

The authors express their gratitude to E. N. Nozdrina for assistance with the measurements.

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named after M. V. Lomonosov

Received
26 VI 1968

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