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Exciton Screening in Amorphous Mg-Bi and Mg-Sb Alloys*

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The Mg $L_{\mathrm{II,III}}$ absorption edge ($h\nu = 50$ eV) has been studied as a function of composition in amorphous Mg-Bi and Mg-Sb alloys using a synchrotron source and a high-resolution grazing-incidence spectrometer. Exciton lines occur and are most prominent for low-conductivity material, e.g., corresponding to $\mathrm{Mg_3Bi_2}$. Screening of the electron-hole interaction takes place as the conductivity increases, but a remnant enhancement remains at threshold even in pure Mg metal.

Certain intermetallic compounds exhibit striking composition-dependent electrical properties when in the liquid or amorphous state. For example, Ferrier and Herrell[1,2] have shown that the electrical conductivity of amorphous $\mathrm{Mg}_x\mathrm{Bi}_{1-x}$ and of $\mathrm{Mg}_x\mathrm{Sb}_{1-x}$ is quite low and cusplike at $x = 0.60$ (e.g., amorphous $\mathrm{Mg_3Bi_2}$) and rises to metallic values on either side of this composition. We find that sharp exciton lines occur at the Mg $L_{\mathrm{II,III}}$ absorption edge in the extreme ultraviolet (50 eV) for low-conductivity amorphous films. These exciton lines tend to be screened out with increasing conductivity, but a remnant enhancement remains at threshold even in pure Mg metal.

The spectra were obtained by measuring the transmission of synchrotron radiation through thin films using a high-resolution grazing-incidence monochromator.[3] The amorphous films (90–510 Å thickness) were made *in situ* by coevaporation onto Formvar substrates kept near 100°K by baffles at liquid-nitrogen temperature. Composition x could be controlled to about 1 or 2% by means of crystal thickness monitors and circuitry developed to display accurately the ratio of evaporant fluxes. Thermal flux was minimized by means of baffles and large source-to-substrate distances (1 m). The amorphous Mg-Bi alloys could be transformed to crystalline simply by slowly warming to room temperature.

Figure 1 shows the absorption spectra for several amorphous $\mathrm{Mg}_x\mathrm{Bi}_{1-x}$ films of different composition x. The instrument spectral bandwidth was less than 0.02 eV. These spectra are all

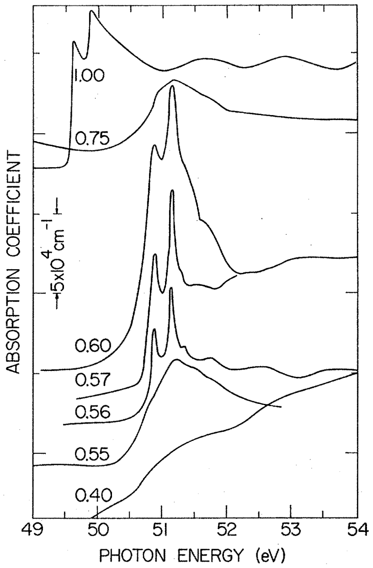

FIG. 1. Absorption coefficient versus photon energy for Mg_xBi_{1-x} at 100°K. All samples were amorphous except magnesium metal, $x=1.00$. The same scale applies to all spectra, but the curves have been shifted arbitrarily along the vertical axis for clarity in display.

drawn to the same vertical scale, but are displaced along the vertical axis for purposes of clarity. Note the strong resonances near $x=0.6$ (low conductivity) due to two spin-orbit-split $n=1$ exciton transitions from the Mg $2p^6$ core. The intensities of the resonances at threshold are comparable to the edge enhancement in pure Mg metal ($x=1.00$) shown at the top of Fig. 1. On the other hand, the shape and *relative* strength of the two spin-orbit components is very different between the metallic and insulating case. For Mg metal the observed splitting is 0.258 ± 0.01 eV and the $j=\frac{3}{2}$ and $j=\frac{1}{2}$ components are in the ratio 2 : 1. At $x=0.6$ the intensity ratio is about 1 : 1.4 (uncertainty of about 10%). This lower ratio for amorphous Mg_3Bi_2 is due to electron-hole exchange as discussed by Onodera and Toyozawa[4] and observed for core excitons in the magnesium halides by Rabe *et al.*[5] Here the exchange effects are appreciable but less than in the halide crystals. The observed exciton splitting in amorphous $Mg_{0.6}Bi_{0.4}$ is 0.269 ± 0.01 eV and must be only slightly larger than the spin-orbit splitting.

A simple argument can be given for the screening of excitons. Let the electron-hole potential be given by[6]

$$U = -(e^2/\epsilon r)e^{-\lambda r}, \tag{1}$$

where the classical screening length $1/\lambda$ is given by

$$1/\lambda = (\epsilon kT/4\pi e^2 n_0)^{1/2}. \tag{2}$$

Here n_0 is the carrier density which might be estimated from the conductivity of films whose compositions are those over which distinct exciton lines occur. Figure 1 indicates that this range is bounded by $x=0.65$ and $x=0.55$, and the corresponding conductivity in both cases[1] is $\sigma \sim 100\ \Omega^{-1}\ \mathrm{cm}^{-1}$. Assuming a mobility $\mu \sim 100$ cm²/V sec (nonhopping) yields an n_0 of 10^{19} cm^{-3}. At $T=90$°K Eq. (2) then gives a screening length of 2–6 Å for dielectric constants ϵ in the range 1–9. This can be compared with an exciton radius estimated from the optical data, where the observed intensity ratio and exchange effects indicate compact exciton states. Furthermore, the structure seen on the high-energy sides of the lines of Fig. 1 for compositions x near 0.6 is likely due to transitions to the $n=2$ exciton states. From the difference in $n=1$ and $n=2$ exciton energies, we estimate an exciton Rydberg of 0.74 ± 0.08 eV and a Bohr radius of about 2.3 Å. Effective screening might therefore take place for carrier densities of the order of magnitude quoted above.

A more complete theory of x-ray excitons and the transition from insulating to metallic behavior has been given by Combescot and Nozières.[7] These authors show, using a very approximate potential, that the familiar exciton line of an insulator broadens asymmetrically towards higher energy as conductivity increases, ultimately transforming into the "infrared singularity" observed in the case of some metals.[8,9] This broadening can be described as a kind of Auger process in which many electron-hole pairs at the Fermi surface accompany the core excitation.[10] It is characteristic of these theories that the response or transition probability $W(E)$ depends upon photon energy E, above threshold E_0, as

$$W(E) \propto (E-E_0)^{-\alpha}. \tag{3}$$

Actually, the spectrum may have a singularity at threshold or no discontinuity at all depending upon whether the critical exponent α is positive or negative. For example, our measurements on the L shell of Mg metal, shown in the upper part of Fig. 1, indicate that α is positive 0.35. The exponent is also positive for excitation of the L shell of Na and Al. In the case of the K-shell excitation of Li the coefficient α is negative and the edge diminished rather than enhanced.[8] When amorphous Mg_xBi_{1-x} is heated above where it crystallizes the conductivity increases and is greater than 700 Ω^{-1} cm^{-1} for all values of x. We observe that the exciton resonances for $x = 0.6$ disappear upon crystallization and do not reappear upon recooling. Presumably the critical exponent in crystalline Mg_3Bi_2 is such as to give diminution rather than enhancement.

Amorphous Mg_xSb_{1-x} is very resistive over a much wider range of composition than Mg_xBi_{1-x}. The conductivity of the antimonide is less than 1×10^{-3} Ω^{-1} cm^{-1} for compositions in the range $0.4 < x < 0.6$ where strong excitonic enhancement is found. For $x = 0.6$, spin-orbit–split exciton lines are observed at 51.25 and 51.50 (± 0.05) eV with an intensity ratio of approximately 1 : 1.5. These lines are somewhat broader and less well-resolved than in Mg-Bi. The $n = 2$ exciton components are not clearly seen either because of additional damping or because the exciton is a little less strongly bound in the antimonide. Outside of the range $0.4 < x < 0.6$, a more or less continuous transition to the screened case (shape like that for $x = 0.55$ or $x = 0.75$ in Fig. 1) takes place, in contrast to the abrupt change argued for quite a different system by Raz *et al.*[11]

By fitting Eq. (3) to our data, we can obtain exponents α for comparison with theory. This can be done because of good signal-to-noise ratio and the fact that, except in the most insulating case, the curves have a steeper rising than falling part. Account must be taken of the splitting, and the trailing portions of each component are plotted on a $\log\alpha$ versus $\log E$ basis. Figure 2 shows the values of α obtained in this way for amorphous Mg_xSb_{1-x} together with resistivity *versus* composition as measured by Ferrier and Herrell.[2] Notice that α peaks near a composition $x = 0.6$ where the resistivity rapidly diverges.

In the Nozières theory it is the phase shift δ for scattering of electrons at the Fermi energy which determines the critical exponent α. This phase shift is connected with the critical exponent by the expression $\alpha = (2\delta/\pi) - (\delta/\pi)^2$. Notice that α in Fig. 2 varies continuously over a narrow range, whereas resistivity changes over many orders of magnitude. Now what is needed is a simple expression relating phase shift to screening length or carrier density. Efforts along these lines are underway.[12] The significant features of the present experimental work are that remarkable core exciton effects are found for amorphous Mg-alloy systems, and screening takes place which can be followed continuously from insulating to metallic conductivities.

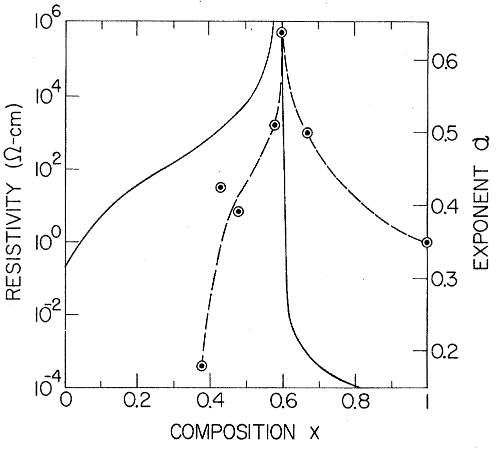

FIG. 2. The solid curve (log scale on the left) shows resistivity (Refs. 1 and 2) of amorphous Mg_xSb_{1-x} as a function of composition x. Critical exponents α are indicated by the dashed curve with data points and linear scale on the right.

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Hall Effect of Silver Ions in $RbAg_4I_5$ Single Crystals

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The Hall effect of the high ionic conductor $RbAg_4I_5$ was studied from 0 to 40°C. By comparison with the results on photoexcited carriers, it is determined that the origins of Hall signals in $RbAg_4I_5$ are the mobile silver ions. The value of Hall mobility is about 0.05 $cm^2\ V^{-1}\ sec^{-1}$ at room temperature, which is about 30 times as large as that of the ions in NaCl at 780°C previously obtained by Read and Katz.

There have been many Hall-effect studies concerning the electrons and the holes in ionic crystals and semiconductors by using various techniques.[1] However, no previous study has been conducted on the Hall effect of ions in a solid except for one in NaCl single crystals at a high temperature by Read and Katz[2]; the sodium ions were supposed to be the primary origin of the voltage. Hall-effect measurements of ions in a solid are very difficult, because it is suspected that the ionic carriers spend an appreciable time in a stable status in the lattice and that they possess very heavy masses and very large volumes compared with those of electronic carriers. Furthermore, the space charge near the electrodes arising from the movement of ions under an electric field causes additional difficulties in taking measurements.

Recently, several scientists[3] investigated high-ionic-conducting solid electrolyte rubidium silver iodide $RbAg_4I_5$, which has an ionic conductivity of about 0.2 $\Omega^{-1}\ cm^{-1}$ at room temperature. Using the Tubandt method, it was determined that the charge-carrying species in $RbAg_4I_5$ were the silver ions and their transport number was about 0.995.[4] This high ionic conductivity was assigned mainly due to the isostructural lattice of $RbAg_4I_5$. The purpose of this work is to study the behavior of silver ions in $RbAg_4I_5$ single crystals by Hall-effect measurements.

The Hall effect in $RbAg_4I_5$ was investigated by a new technique[5] which was essentially an ac method to prevent the accumulation of space charges near electrodes; the alternating current $I(f_1)$ through a sample and the alternating applied magnetic field $H(f_2)$ were phase locked to each other. Thus, the observed Hall voltage oscillated with a frequency of the sum or the difference of f_1 and f_2. Actually, f_1 and f_2 were 75 and 50 Hz, respectively. A component with 125 Hz in the Hall voltage was selected and amplified by a low-noise preamplifier with a pass filter followed by a lock-in amplifier. Square-shaped samples with four electrodes were investigated over a temperature range from 0 to 40°C. It was confirmed that the measuring system used in this experiment was able to detect a Hall voltage as low as around 1 nV, about 50 times as sensitive as the method used by Read and Katz.[2] The validity of this technique was confirmed by performing the same measurements on *n*-type Ge specimens whose electronic properties were studied by independent experiments.

Single crystals of $RbAg_4I_5$ as large as 1 cm diam × 4 cm long were grown from melts by the Czochralski technique.[6] Extrapure reagents AgI and RbI were purified by vacuum distillation and then by zone melting. The crystals obtained were transparent with a light yellow tint. Sizes of the specimens were about $6\times6\times0.5\ mm^3$.

Hall voltages in $RbAg_4I_5$ single crystals in the dark are linear with respect to the applied fields —both magnetic and electric. Hall mobility μ_c in the dark is shown in Fig. 1 as a function of the reciprocal temperature. The value of μ_c increases with increasing temperature, and is about 0.05 $cm^2\ V^{-1}\ sec^{-1}$ at room temperature which is approximately 30 times as large as that of the ions in NaCl single crystals at 780°C obtained by Read and Katz.[2]

Measurements of the Hall effect and conductivity under photoexcitation were effected to confirm that origins of the Hall data presented in Fig. 1 were the silver ions in $RbAg_4I_5$. Since the wave-